

AIR MONITORING FOR HAZARDOUS MATERIALS

(165.4)

5 Days

This course instructs participants in the practices and procedures for monitoring and sampling airborne hazardous materials. It is designed for personnel who evaluate releases of airborne hazardous materials at hazardous waste sites or accidental hazardous material releases.

Topics that are discussed include air monitoring and sampling programs, air monitoring and sampling techniques, air monitoring and sampling equipment, instrument calibration, exposure guidelines, air dispersion modeling, and health and safety considerations. The course will include operating procedures for specific air monitoring and sampling equipment, as well as strategies for air monitoring and sampling at abandoned hazardous waste sites and for accidental releases of hazardous chemicals.

Instructional methods include a combination of lectures, group discussions, problem-solving sessions, and laboratory and field exercises with hands-on use of instruments.

After completing the course, participants will be able to:

- Properly use the following types of air monitoring and sampling equipment:
 - Combustible gas indicators
 - Oxygen monitors
 - Detector tubes
 - Toxic gas monitors
 - Photoionization detectors
 - Flame ionization detectors
 - Gas chromatographs
 - Sampling pumps
 - Direct-reading aerosol monitors.
- Identify the operational parameters, limitations, and data interpretation requirements for the instruments listed above.
- Identify the factors to be considered in the development of air monitoring and sampling plans.
- Discuss the use of air monitoring data for the establishment of personnel and operations health and safety requirements.

U.S. Environmental Protection Agency
Office of Emergency and Remedial Response
Environmental Response Team

CONTENTS

	<u>Section</u>
Acronyms and Abbreviations	
Air Monitoring Plans and Strategies	1
Exposure Limits and Action Levels	2
Oxygen Monitors, Combustible Gas Indicators, and Specific Chemical Monitors	3
Total Vapor Survey Instruments	4
Air Sample Collection	5
Introduction to Gas Chromatography	6
Air Dispersion Modeling During Emergency Response	7
References	8
Manufacturers and Suppliers of Air Monitoring Equipment	9
Workbook: Air Monitoring for Hazardous Materials	10

ACRONYMS AND ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
AID	argon ionization detector
AIHA	American Industrial Hygiene Association
ALOHA	areal locations of hazardous atmospheres
ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
BEI	biological exposure indices
C	ceiling (precedes exposure limit)
cc/min	cubic centimeters per minute
cfm	cubic feet per minute
CFR	Code of Federal Regulations
CGI	combustible gas indicator
Cl	chlorine
CO	carbon monoxide
DNPH	2,4-dinitrophenylhydrazine
DQO	data quality objective
ECD	electron capture detector
EPA	U.S. Environmental Protection Agency
ERT	Environmental Response Team (EPA)
eV	electron volt
FID	flame ionization detector
FM	Factory Mutual Research Corporation
GC	gas chromatography
HCl	hydrogen chloride
ICS	incident command system
IDLH	immediately dangerous to life or health
IP	ionization potential
KOH	potassium hydroxide
LCD	liquid crystal display
LED	light-emitting diode
LEL	lower explosive limit
LFL	lower flammable limit
lpm	liters per minute

MACs	maximum allowable concentrations
MAKs	maximum concentrations at the workplace (Federal Republic of Germany)
MCE	mixed cellulose ester
mg/m ³	milligrams per cubic meter
ml	milliliter
mm	millimeter
MOS	metal-oxide semiconductor
MSDS	material safety data sheets
MSHA	Mine Safety and Health Administration
NaOH	sodium hydroxide
NEC	National Electrical Code
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
NRC	Nuclear Regulatory Commission
OH	hydroxide
OSHA	Occupational Safety and Health Administration
OVA	organic vapor analyzer (Foxboro®)
OVN	organic vapor meter
PAH	polycyclic (or polynuclear) aromatic hydrocarbon
PBK	playback
PCB	polychlorinated biphenyl
PEL	permissible exposure limit
PID	photoionization detector
ppb	parts per billion
PPE	personal protective equipment
ppm	parts per million
ppt	parts per trillion
PUF	polyurethane foam
PVC	polyvinyl chloride
REL	recommended exposure limits
SA	shift average
SCBA	self-contained breathing apparatus
SEI	Safety Equipment Institute
SOP	standard operating procedure
SOSG	Standard Operating Safety Guides
SS	chemical-specific sensor
STEL	short-term exposure limit
TCD	thermal conductivity detector
TLV	threshold limit values
TWA	time-weighted average

UEL	upper explosive limit
UL	Underwriters' Laboratory, Inc.
UV	ultraviolet light
VDC	volts DC
WEEL®	workplace environmental exposure level

AIR MONITORING PLANS AND STRATEGIES

PERFORMANCE OBJECTIVES

At the end of this lesson, participants will be able to:

- List six objectives of air monitoring specified by the EPA *Standard Operating Safety Guides*
- Identify the OSHA standard and EPA standard that cover hazardous waste site operations and emergency response
- List four situations that initial entry monitoring is designed to detect
- Differentiate between "personal monitoring" and "area monitoring"
- Define, per 1910.120, when personnel monitoring is required
- List documents that EPA has developed as guidance for compliance with 1910.120
- Given the *Personal Air Sampling and Air Monitoring Requirements Under 29 CFR 1910.120* fact sheet, define air monitoring and air sampling
- List three uses of meteorological data.

AIR MONITORING PLANS AND STRATEGIES

AIR MONITORING EPA Objectives

- Identify and quantify airborne contaminants onsite and offsite
- Track changes in air contaminants that occur over the lifetime of the incident
- Ensure proper selection of work practices and engineering controls

Source: EPA SOSGs

AIR MONITORING EPA Objectives

- Determine the level of worker protection needed
- Assist in defining work zones
- Identify additional medical monitoring needs in any given area of the site.

Source: EPA SOSGs

NOTES

WORKER PROTECTION STANDARDS (OSHA)

- 29 CFR 1910.120 (HAZWOPER)
- Applies to
 - Federal employees
 - Private industry employees
 - State and local employees in OSHA states

WORKER PROTECTION STANDARDS (EPA)

- 40 CFR Part 311
- Applies to state and local employees in non-OSHA states
- Wording same as 1910.120

MONITORING REQUIREMENTS

NOTES

INITIAL ENTRY

Monitoring for:

- Immediately dangerous to life or health (IDLH) conditions
- Exposures over permissible exposure limits (PELs) or published exposure levels

INITIAL ENTRY

Monitoring for:

- Exposure over a radioactive material's dose limits
- Other dangerous conditions
 - Flammable atmospheres
 - Oxygen-deficient environments

PERIODIC MONITORING

"Periodic monitoring (shall) be done when the possibility of a dangerous condition has developed or when there is reason to believe that exposures may have risen above PELs since prior monitoring was conducted."

Source: EPA SOSGs

NOTES

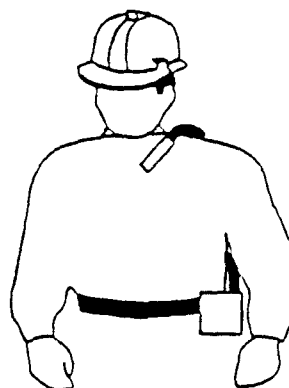
PERSONAL MONITORING

Required

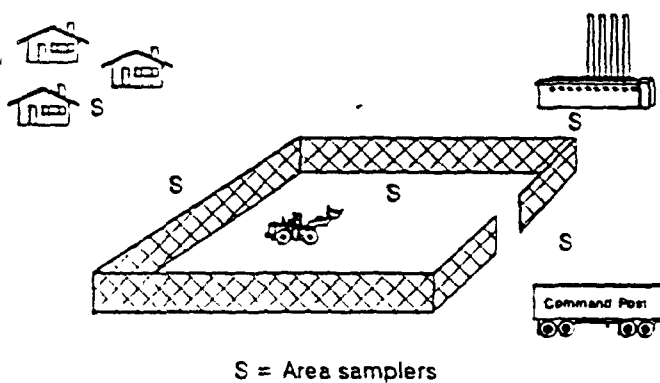
- During actual cleanup phase
- To evaluate high-risk employees (i.e., employees likely to have highest exposures)
- Evaluation of other employees needed if high-risk employees exceed exposure limits

Source: 1910.120(h)(4)

PERSONAL MONITORING



AREA MONITORING



NOTES

SITE SAFETY AND HEALTH PLAN

Minimum requirement

"Frequency and types of air monitoring, personnel monitoring, and environmental sampling techniques and instrumentation to be used, including methods of maintenance and calibration of monitoring and sampling equipment to be used."

Source: 1910.120(b)(4)(ii)(E)

GUIDANCE DOCUMENTS OSHA

- Technical manual
- Analytical methods manual

GUIDANCE DOCUMENTS EPA

- EPA-ERT *Standard Operating Safety Guides (SOSGs)*, Publication 9285.1-03, June 1992
- *Personal Air Sampling and Air Monitoring Requirements (PASAMR)* Under 29 CFR 1910.120 fact sheet, Publication 9360.8-17FS, May 1993

NOTES

AIR MONITORING vs. AIR SAMPLING

- Air monitoring refers to the use of direct-reading instruments producing instantaneous data
- Air sampling refers to the use of a sampling pump and collection media that produce samples that must be sent to a laboratory for analysis

AIR MONITORING Features

- "Real time" (direct reading)
- Rapid response
- Generally not compound specific
- Limited detection levels
- May not detect certain classes of compounds

AIR SAMPLING Features

- Compound or class specific
- Greater accuracy
- Requires more time for results
- Requires additional pumps, media, and analytical support

NOTES

PERSONNEL AIR SAMPLING Elements in Sampling Strategy

- Employee sampled
- Tasks performed
- Duration
- Hazardous substances
- Equipment to be used

Source: PASAMR fact sheet

AREA SAMPLING Locations

- Upwind
 - Establish background
- Support zone
 - Ensure support area is clean and remains clean

Source: EPA SOSGs

AREA SAMPLING Locations

- Contamination reduction zone
 - Ensure that personnel in zone are properly protected
 - Ensure that onsite workers are not removing PPE in a contaminated area

Source: EPA SOSGs

NOTES

AREA SAMPLING Locations

- Exclusion zone
 - Represents greatest risk of exposure
 - Requires most sampling
 - Use data to set boundaries
 - Use data to select proper levels of PPE
 - Provide a record of air contaminants

Source: EPA SOSGs

AREA SAMPLING Locations

- Fenceline/downwind
 - Determine whether air contaminants are migrating from site

Source: EPA SOSGs

AREA SAMPLING Elements in Sampling Strategy

- Locations where air sampling will be performed
- Hazardous substances that will be sampled during the task
- Duration of the sample

Source: PASAMR fact sheet

NOTES

AREA SAMPLING Elements in Sampling Strategy

- Equipment that will be used to sample for the different hazardous substances
- Collection of meteorological data

Source: PASAMR fact sheet

METEOROLOGICAL CONSIDERATIONS

- Data needed
 - Wind speed and direction
 - Temperature
 - Barometric pressure
 - Humidity

METEOROLOGICAL CONSIDERATIONS

- Data uses
 - Placement of samplers
 - Input for air models
 - Calibration adjustments
- Data sources
 - Onsite meteorological stations
 - Government or private organizations

NOTES

AIR DISPERSION MODELS

- Public exposure assessment
- Air monitoring and air modeling should interact

LONG-TERM AIR MONITORING PROGRAMS

Considerations

- Type of equipment
- Cost
- Personnel
- Accuracy of analysis
- Time to obtain results
- Availability of analytical laboratories

Source: EPA SOSGs

LONG-TERM AIR MONITORING PROGRAMS

ERT Approach

- Use total vapor survey instruments for organic vapors and gases
 - Initial detection
 - Periodic site surveys
 - Area monitors to track changes

Source: EPA SOSGs

LONG-TERM AIR MONITORING PROGRAMS

ERT Approach

- Collect air samples
 - Analyze with field gas chromatographs
 - Send selected samples to laboratories
- Use survey instruments or gas chromatographs to screen samples for laboratory analysis

Source: EPA SOSGs

LONG-TERM AIR MONITORING PROGRAMS

ERT Approach

- When they are known to be present or when there are indications that they may be a problem, sample for
 - Particulates
 - Inorganic acids
 - Aromatic amines
 - Halogenated pesticides

Source: EPA SOSGs

ADDITIONAL READING

- Air/Superfund Technical Guidance Study Series
 - Volume IV - *Guidance for Ambient Air Monitoring at Superfund Sites* (revised), EPA-451/R-93-007, May 1993
 - *Compilation of Information on Real-Time Monitoring for Use at Superfund Sites*, EPA-451/R-93-008, May 1993

NOTES

INSTRUMENT CHARACTERISTICS

SELECTIVITY

- Selectivity is an instrument's ability to differentiate a chemical from others in a mixture
- Chemicals that affect an instrument's selectivity are called interferences

SENSITIVITY

Sensitivity is the least change in concentration that will register an altered reading of the instrument

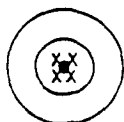
Source: Air Sampling and Analysis for Contaminants: An Overview

NOTES

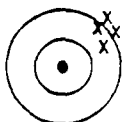
ACCURACY AND PRECISION

- Accuracy refers to the difference between the instrument reading and the true or correct value.
- Precision is the grouping of the data points around a calculated average. Precision measures the repeatability of data.

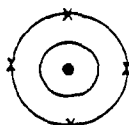
ACCURACY AND PRECISION



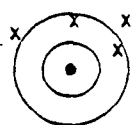
Accurate and Precise



Precise but Inaccurate



Accurate but Imprecise



Inaccurate and Imprecise

Source: *The Industrial Environment - Its Evaluation and Control*

RELATIVE RESPONSE

- Relative response is the relationship between an instrument's reading and the actual concentration
- Calculation

$$\text{Relative Response} = \frac{\text{Instrument Reading}}{\text{Actual Concentration}}$$

NOTES

CALIBRATION

- Process of checking an instrument to see if it gives the proper response and making any necessary adjustments.
- Direct-reading instruments generally are calibrated to one chemical (the standard).

RESPONSE TIME

- Response time is the time between initial sample contact and readout of the full chemical concentration (usually seconds to minutes)
- Turnaround time is the time from sample collection to receipt of results (days to weeks)

MOBILITY

- Portable
 - Hand held
 - No external power supply
- Fieldable
 - Particularly rugged
 - Easily transported by vehicle
 - Limited external power supply
- Mobile
 - Small enough to carry in a mobile lab

Source: Field Screening Methods Catalog, EPA/540/2-88/005, September 1988

NOTES

EASE OF OPERATION

- How easy is it to operate the controls?
- How easy is it to learn to operate?
- How many steps must be performed before an answer is obtained?
- How easy is it to repair?

INHERENT SAFETY



APPROVED



32L6

LISTED

INTRINSICALLY SAFE COMBINATION

COMBUSTIBLE GAS AND OXYGEN INDICATING

DETECTOR FOR HAZARDOUS LOCATIONS

CLASS I, DIVISION 1, GROUPS A, B, C & D

Source: Scott Model S-105 Certification Label

AIR MONITORING PLANS AND STRATEGIES

INTRODUCTION

Airborne contaminants present at a hazardous waste site or a hazardous materials release can present a risk to human health and the environment. One way to assess that risk is to identify and quantify these contaminants by air monitoring. The U.S. Environmental Protection Agency's (EPA) *Standard Operating Safety Guides* (SOSGs) state that the objectives of air monitoring during response operations are to:

- Identify and quantify airborne contaminants onsite and offsite
- Track changes in air contaminants that occur over the lifetime of the incident
- Ensure proper selection of work practices and engineering controls
- Determine the level of worker protection needed
- Assist in defining work zones
- Identify additional medical monitoring needs in any given area of the site.

Several questions should be addressed when you develop an air monitoring plan. *Why* is the air monitoring being done? *How* will the monitoring be done? *Who* will do the monitoring? *When* and *where* will the air monitoring be done? *What* equipment will be used?

The above list gives several reasons why air monitoring is done. Some organizations have developed guidelines on the why, how, who, where, when, and what of air monitoring. Some organizations have procedures that are legal requirements. These organizations will be discussed. Also, general equipment characteristics will be covered in the latter part of this section.

STANDARDS AND GUIDELINES

U.S. Department of Labor - Occupational Safety and Health Administration (OSHA)

Since 1971, OSHA has regulated exposure to chemicals in industry. 29 CFR Part 1910.1000 specifies limits on exposure to airborne concentrations of chemicals. See the section on *Exposure Limits and Action Levels* for further information.

On March 6, 1990, OSHA's *Hazardous Waste Operations and Emergency Response* standard (29 CFR Part 1910.120) went into effect. This standard addressed the legal requirements for protecting workers involved with hazardous waste or emergency responses to hazardous materials. Air monitoring is one of the many activities regulated by this standard.

The standard requires the site-specific safety and health plan to address:

Frequency and types of air monitoring, personnel monitoring, and environmental sampling techniques and instrumentation to be used, including methods of maintenance and calibration of monitoring and sampling equipment to be used. {1910.120(b)(4)(ii)(e)}.

Under section (c) *Site characterization and analysis* is:

(6) *Monitoring*. The following monitoring shall be conducted during initial site entry when the site evaluation produces information that shows the potential for ionizing radiation or IDLH (*Immediately Dangerous to Life or Health*) conditions, or when the site information is not sufficient reasonably to eliminate these possible conditions:

(i) Monitoring with direct-reading instruments for hazardous levels of radiation.

(ii) Monitoring the air with appropriate direct-reading test equipment (e.g., combustible gas meter, detector tubes) for IDLH and other conditions that may cause death or serious harm (combustible or explosive atmospheres, oxygen deficiency, toxic substances).

(iii) Visually observing for signs of actual or potential IDLH or other dangerous conditions.

(iv) An ongoing air monitoring program in accordance with paragraph (h) of this section shall be implemented after site characterization has determined the site is safe for the startup of operations.

This section states when monitoring should be done (site entry), why it is done (to identify IDLH conditions), and what kind of equipment to use. Additional requirements are found under (h) *Monitoring*.

(1) *General*

(i) Monitoring shall be performed in accordance with this paragraph where there may be a question of employee exposure to hazardous concentrations of hazardous substances in order to assure proper selection of engineering controls, work practices and personal protective equipment so that employees are not exposed to levels which exceed permissible exposure limits or published exposure levels for hazardous substances.

(ii) Air monitoring shall be used to identify and quantify airborne levels of hazardous substances and safety and health hazards in order to determine the appropriate level of employee protection needed on site.

Here the purpose (why) is to identify and quantify hazardous substances so that proper exposure controls are used. The substances are identified and quantified so that the concentrations can be compared to an exposure limit. See the *Exposure Limits and Action Levels* section for further information on exposure limits.

(2) *Initial entry.* Upon initial entry, representative air monitoring shall be conducted to identify any IDLH condition, exposure over permissible exposure limits or published exposure levels, exposure over a radioactive material's dose limits or other dangerous condition such as the presence of flammable atmospheres or oxygen-deficient environments.

This paragraph expands on site characterization and analysis paragraph (c)(6) by including exposure limits along with IDLH conditions to monitor.

(3) *Periodic monitoring.* Periodic monitoring shall be conducted when the possibility of an IDLH condition or flammable atmosphere has developed or when there is indication that exposures may have risen over permissible exposure limits or published exposure levels since prior monitoring. Situations where it shall be considered whether the possibility that exposures have risen are as follows:

- (i) When work begins on a different portion of the site.
- (ii) When contaminants other than those previously identified are being handled.
- (iii) When a different type of operation is initiated (e.g., drum opening as opposed to exploratory well drilling).
- (iv) When employees are handling leaking drums or containers or working in areas with obvious liquid contamination (e.g., a spill or lagoon).

Again, where, when, and why are covered.

(4) *Monitoring of high-risk employees.* After the actual cleanup phase of any hazardous waste operation commences; for example, when soil, surface water, or containers are moved or disturbed; the employer shall monitor those employees likely to have the highest exposure to hazardous substances and health hazards likely to be present above permissible exposure limits or published exposure levels by using personal sampling frequently enough to characterize employee exposures. If the employees likely to have the highest exposure are over permissible exposure limits or published exposure limits, then monitoring shall continue to determine all employees likely to be above those limits. The employer may utilize a representative sampling approach by documenting that the employees and chemical chosen for monitoring are based on the criteria stated above.

Note to (h): It is not required to monitor employees engaged in site characterization operations covered by paragraph (c) of this section.

These paragraphs state that personal monitoring (how) must be done on high-risk employees (who) during cleanup activities (when).

Section (q) of 1910.120 addresses emergency responses to hazardous substance releases. It states in (q)(3)(ii) that

the individual in charge of the ICS (*Incident Command System*) shall identify, to the extent possible, all hazardous substances or conditions present and shall address as appropriate site analysis, use of engineering controls, maximum exposure limits, hazardous substances handling procedures, and use of any new technologies.

Air monitoring is not specifically mentioned in section (q), but would be a useful, if not necessary, tool for assessment.

29 CFR 1910.120 is a federal regulation. In states where there is an approved state OSHA (state-plan state), requirements at least as stringent as 1910.120 must be developed. Thus, in some states the air monitoring requirements may be more detailed.

U.S. Environmental Protection Agency (EPA)

On June 23, 1989, EPA adopted 40 CFR Part 311, *Worker Protection Standards for Hazardous Waste Operations and Emergency Response*. This standard is a duplicate of 1910.120. The difference in the standards is to whom they apply. The OSHA standard applies to federal agencies, private industries, and public employees in OSHA state-plan states. The EPA standard applies to public employees in states that have no OSHA state-plan.

As noted in the previous paragraph, EPA has regulations for monitoring for worker protection. There are also requirements for monitoring for public protection. However, this subject will not be discussed here in detail. Additional information is mentioned in this manual in the *Exposure Limits and Action Levels* section.

EPA has published guidelines for hazardous material operations which include air monitoring procedures. General guidelines can be found in the SOSGs. The following topics are discussed in the SOSGs:

1. Objectives of air monitoring
2. Identifying airborne contaminants
3. Air sampling equipment and media
4. Sample collection and analysis
5. General monitoring practices
6. Meteorological considerations
7. Long-term air monitoring programs
8. Variables in hazardous waste site air monitoring
9. Using vapor/gas concentrations to determine level of protection.

Other EPA guidance documents are:

- *Personal Air Sampling and Air Monitoring Requirements Under 29 CFR 1910.120* fact sheet
- *Guidance for Ambient Air Monitoring at Superfund Sites*, Volume IV in the Air/Superfund National Technical Guidance Series
- *Compilation of Information on Real-Time Monitoring for use at Superfund Sites*
- *Removal Program Representative Sampling: Air*
- *A Compendium of Superfund Field Operations Methods*.

EPA's Environmental Response Team (ERT) has developed standard operating procedures for their air monitoring equipment and strategies. These documents provide information on the why, how, when, where, and what of air monitoring. Because EPA is concerned with offsite migration and public exposure along with worker protection, their sampling requirements are broader than OSHA's. Air monitoring is done onsite to determine the type and quantity of chemicals being released. Downwind monitoring is done to determine offsite migration. Upwind sampling is done to determine what background concentrations may be contributing to the downwind and onsite measurements. This helps determine what the site is contributing to the environment.

Some of the methods use air monitoring equipment to monitor for the presence of chemicals in media other than air (e.g., soil gas sampling and water headspace).

Other Organizations

The National Institute for Occupational Safety and Health (NIOSH), the American Conference of Governmental Industrial Hygienists (ACGIH), the American Industrial Hygiene Association (AIHA), and the American Society for Testing and Materials (ASTM) have publications about air monitoring strategies. See the *References* section of this manual for more information.

CHARACTERISTICS OF AIR MONITORING INSTRUMENTS

The selection of equipment to be used must be part of the air monitoring plan. There are many factors to consider when determining the proper equipment to use. Specific instrument characteristics related to the following factors can be found in later sections of this manual.

Hazard

The proper equipment must be selected to monitor the hazard or chemical at hand.

Selectivity

Selectivity is the ability of an instrument to detect and measure a specific chemical. If other chemicals are detected, they are called interferences. Interferences can affect the accuracy of the instrument reading. In some situations, an instrument (like the combustible gas indicator [CGI]) that

responds to more than one chemical is desired. Again, the purpose of the monitoring must be considered.

Sensitivity

Sensitivity is important when slight concentration changes can be dangerous. Sensitivity is defined as the ability of an instrument to accurately measure changes in concentration. Therefore, "sensitive" instruments can detect small changes in concentration.

Accuracy

Accuracy is the measure of how close readings are to true values. It is expressed as % bias. For example, if an instrument is tested and the average results are 15% higher than the true concentration, then the instrument is said to have a bias of +15%. NIOSH recommends that a portable direct-reading instrument be within 25% of the true value 95% of the time.

Precision

Precision is the grouping of the data points. It is a quantitative measure of the variability of a group of measurements compared to their average value. It is defined by the standard deviation. This value is a \pm qualifier when a value is reported (e.g., 10 ± 1 ppm).

Accuracy and precision are affected by factors such as the instrument's calibration and relative response.

Calibration

An instrument must be properly calibrated, prior to use, in order to function properly in the field. Calibration is the process of adjusting the instrument readout so that it corresponds to an actual concentration. Calibration involves checking the instrument results with a known concentration of a gas or vapor to see that the instrument gives the proper response. For example, if a combustible gas meter is checked with a calibration gas that is 20% of the lower explosive limit (LEL), then the instrument should read 20% of the LEL. If it does not read accurately, it is out of calibration and should be adjusted until an accurate reading is obtained.

Although an instrument is calibrated to give a one-to-one response for a specific chemical (the calibration gas), its response to other chemicals is usually different (see *Relative Response* below). If the calibration is changed for an instrument, its relative responses will also change. Also, the instrument may not give a one-to-one response to the chemical for the full range of detection (see detection range).

Instruments come from the manufacturer calibrated to a specific chemical. The manufacturer supplies information about how to maintain that calibration. If the user wants to change the calibration gas, the manufacturer can supply information on how to do so.

Relative Response

Whereas some instruments may detect more than one chemical, equal concentrations may not give equal response. The relationship between the instrument's response and the actual concentration of the chemical is termed the "relative response." Relative response can be calculated by using the following formula:

$$\text{Relative Response} = \frac{\text{Instrument Reading}}{\text{Actual Concentration}} (\times 100\% \text{ for } \% \text{ Relative Response}).$$

For example, if an instrument reading for a 100 ppm concentration of acetone is 63, then the relative response for that instrument and acetone is 0.63 or 63%. Table 1 gives relative response information for a particular CGI.

**TABLE 1. RELATIVE RESPONSE OF SELECTED CHEMICALS
FOR A CGI CALIBRATED TO PENTANE**

Chemical	Concentration (% LEL)	Meter Response (% LEL)	Relative Response (%)
Methane	50	85	170
Acetylene	50	60	120
Pentane	50	50	100
1,4-Dioxane	50	37	74
Xylene	50	27	54

Source: *Portable Gas Indicator, Model 250 and 260, Response Curves*,
Mine Safety Appliances Company, Pittsburgh, PA.

Relative responses vary with chemical and instrument. The same chemical may have a relative response of 63% for one instrument and 120% response for another. Calibration also affects relative response.

Instruments come from the manufacturer calibrated to a specific chemical. If the instrument is being used for a chemical that is not the calibration standard, then it may be possible to look at the manufacturer's information to get the relative response of that instrument for the chemical. Then the actual concentration can be calculated. For example, if the instrument's relative response for xylene is 0.27 (27%) and the reading is 100 ppm (parts per million), then the actual concentration is 370 ppm ($0.27 \times \text{actual concentration} = 100 \text{ ppm}$; $\text{actual concentration} = 100/0.27 = 370 \text{ ppm}$).

If there is no relative response data for the chemical in question, it may be possible to recalibrate the instrument. If the instrument has adjustable settings and a known concentration is available, the instrument may be adjusted to read directly for the chemical. Because recalibration takes time, this is usually done only if the instrument is going to be used for many measurements of the special chemical.

Detection Range

The operating range is the lower and upper use limits of the instrument. It is defined by the lower detection limit at one end and the saturation concentration at the other end. The lower detection limit is the lowest concentration to which an instrument will respond. It is important to use an instrument with an operating range that will accurately measure the concentration in the range of concern. For example, a CGI could be used to monitor for methane because methane is combustible. However, the upper limit of the CGI is the lower explosive limit (LEL) of the chemical. LEL is the lowest concentration of gas or vapor (in air) that will burn or explode if an ignition source is present at ambient temperatures. In this case, that would be 5% methane. If higher concentrations of methane need to be quantified, another type of instrument would be needed. Also, most CGIs are not sensitive to ppm concentrations. A different instrument would be needed to measure that range.

Some instruments may respond to the chemical for a range of concentrations but not give a consistent response throughout the range. The linear range is the range of concentrations over which the instrument gives response proportional to the chemical concentration.

Response Time

Response time is the time between initial sample contact and readout of the full chemical concentration. In direct-reading instruments, a rapid response time is desired. Response time for direct-reading instruments can be from seconds to minutes. The HNU PI-101 gives 90% of full-scale concentration in 3 seconds. Some hydrogen cyanide detectors may take 90 seconds to give a full concentration reading. Factors that affect response time are temperature, type of detector, and sample hose length.

For methods that require air sample collection and analysis, the response time is referred to as the turnaround time. In other words, how long was the period of time between collection of the sample and receipt of results from the laboratory?

Mobility

EPA's Field Screening Methods Catalog uses the following terms:

- **Portable**—Hand-held devices that can be easily carried by one person and require no external power source.
- **Fieldable**—Easily transported in a van, pick-up, or four-wheel drive. Particularly rugged and limited external power required.
- **Mobile**—Small enough to carry in a mobile lab. Power consideration may limit the use of many instruments in mobile laboratories. (Size, durability, and power supply are the main considerations in determining the mobility of an instrument.)

Ease of Operation

Because many of these instruments were designed for industrial use, allowances may not have been made for using the instrument while wearing protective equipment. One must consider how easy it is to use the instrument while wearing gloves or how difficult it is to read the meter while wearing a respirator. Also, how quickly a user can learn to operate the instrument correctly should be considered.

Preparation time for use of the instrument should be short. Rapid warm-up, easy attachment of accessories, and quick instrument checks shorten preparation time.

Direct-Reading vs. Sample Analysis

Direct-reading instruments are those that give a response to a chemical within seconds or minutes of contact. They are also meant to be taken to the location that is to be evaluated. Sample analysis, however, involves collecting an air sample on a media or in a container and then sending it to an analytical laboratory. This type of analysis involves much more time—sometimes days longer—than using a direct-reading instrument.

Personal vs. Area Monitor/Sampler

A personal monitor/sampler is one that can be worn by the worker with the intent of obtaining the exposure for the wearer. An area monitor/sampler obtains information for the area in which it is placed. A personal monitor/sampler must be small enough to be worn by the worker and also must have a battery supply if it is electronic. A personal monitor/sampler is the ultimate in portability. They range in size from pocket size to a size that can be clipped to a belt without hindering the wearer. Area samplers can be much larger and can use AC power. Many of the personal monitors are equipped with warning alarms and with dataloggers to store and calculate exposures.

Inherent Safety

Many of the instruments used for air monitoring will be used in the atmosphere being monitored. Therefore, they must be safe to use in that environment. Electrical devices, including instruments, must be constructed to prevent the ignition of a combustible atmosphere. The sources of this ignition could be an arc generated by the power source itself or the associated electronics, or a flame or heat source necessary for function of the instrument. The National Fire Protection Association (NFPA) publishes the National Electrical Code (NEC), which spells out types of areas in which hazardous atmospheres can be generated and the types of materials that generate these atmospheres. It also lists design safeguards acceptable for use in hazardous atmospheres.

Hazardous Atmospheres

The term "hazardous atmosphere" causes response workers, depending on their backgrounds, to imagine situations ranging from toxic air contaminants to flammable atmospheres. For NEC purposes, an atmosphere is hazardous if it meets the following criteria:

- It is a mixture of any flammable material in air whose concentration is within the material's flammable range (i.e., between the material's lower flammable limit and its upper flammable limit).
- There is the potential for an ignition source to be present.
- The resulting exothermic reaction could propagate beyond where it started.

To adequately describe hazardous atmospheres, the NEC categorizes them according to their class, group, and division. Class is a category describing the type of flammable material that produces the hazardous atmosphere:

- Class I is flammable vapors and gases, such as gasoline and hydrogen. Class I is further divided into Groups A, B, C, and D on the basis of similar flammability characteristics (Table 2).
- Class II consists of combustible dusts like coal or grain and is divided into groups E, F, and G (Table 3).
- Class III is ignitable fibers such as those produced by cotton milling.

TABLE 2. SELECTED CLASS I CHEMICALS BY GROUP

Group	Examples of Chemicals Within Group		
Group A Atmospheres	acetylene		
Group B Atmospheres	1,3-butadiene	ethylene oxide	hydrogen
Group C Atmospheres	carbon monoxide diethyl ether dicyclopentadiene ethyl mercaptan	ethylene hydrazine hydrogen sulfide methyl ether	nitropropane tetrahydrofuran tetramethyl lead triethylamine
Group D Atmospheres	acetone ammonia benzene ethanol	fuel oils gasoline liquified petroleum gas methane	methyl ethyl ketone propane vinyl chloride xylenes

Source: NFPA. 1991. *Classification of Gases, Vapors, and Dusts for Electrical Equipment in Hazardous (classified) Locations*. National Fire Protection Association, ANSI/NFPA 497M.

TABLE 3. SELECTED CLASS II CHEMICALS BY GROUP

Group	Characteristics of Group
Group E Conductive Dusts	Atmospheres containing metal dusts, including aluminum, magnesium, and their commercial alloys, and other metals of similarly hazardous characteristics
Group F Semivolatile Dusts	Atmospheres containing carbon black, coal, or coke dust with more than 8% volatile material
Group G Nonconductive Dusts	Atmospheres containing flour, starch, grain, carbonaceous, chemical thermoplastic, thermosetting and molding compounds.

Source: NFPA. 1991. *Classification of Gases, Vapors, and Dusts for Electrical Equipment in Hazardous (classified) Locations*. National Fire Protection Association, ANSI/NFPA 497M.

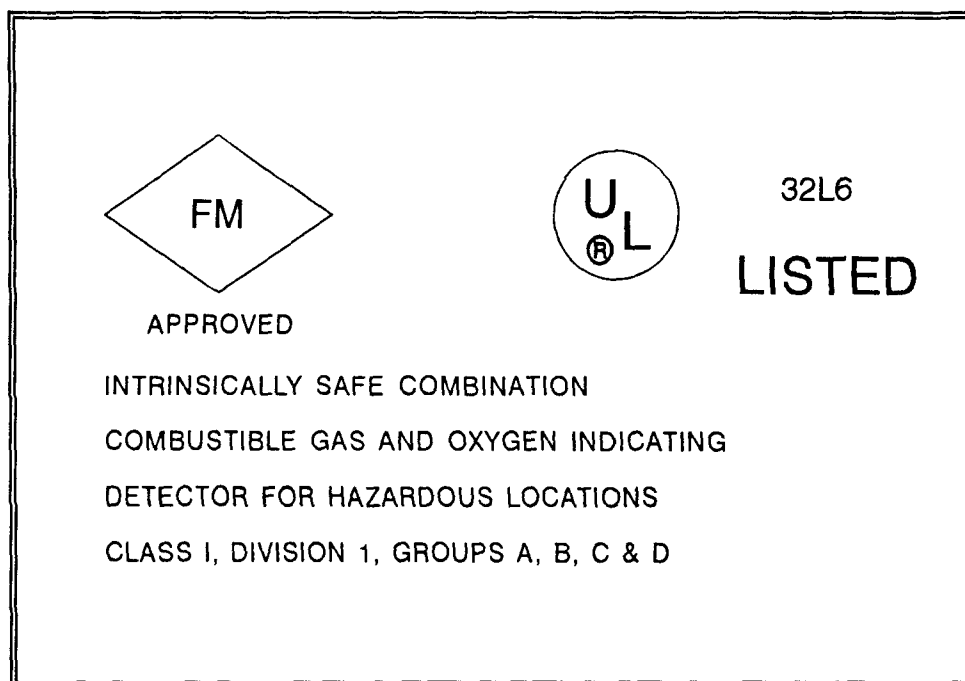
Division is the term describing the "location" of generation and release of the flammable material.

- Division 1 is a location where the generation and release are continuous, intermittent, or periodic into an open, unconfined area under normal conditions. Instruments certified for Division 1 locations are also called "intrinsically safe."
- Division 2 is a location where the generation and release are only from ruptures, leaks, or other failures from closed systems or containers.

Using this system, a hazardous atmosphere can be routinely and adequately defined. As an example, an abandoned waste site containing intact closed drums of methyl ethyl ketone, toluene and xylene would be considered a Class I, Division 2, Group D environment. However, when transfer of the flammable liquids takes place at the site, or if releases of flammable gases/vapors are considered normal, those areas would be considered Class I, Division 1.

Certification

If a device is certified for a given class, division, and group, and it is used, maintained, and serviced according to the manufacturer's instructions, it will not contribute to ignition. The device is not, however, certified for use in atmospheres other than those indicated. All certified devices must be marked to show class, division, and group (**Figure 1**). Any manufacturer wishing to have an electrical device certified must submit a prototype to a recognized laboratory for testing. If the unit passes, it is certified as submitted. However, the manufacturer agrees to allow the testing laboratory to randomly check the manufacturing plant at any time, as well as any marketed units. Furthermore, any change in the unit requires the manufacturer to notify the test laboratory, which can continue the certification or withdraw it until the modified unit can be retested. NFPA does not do certification testing. Testing and certification is done by such organizations as Underwriters' Laboratory, Inc. (UL) or Factory Mutual Research Corporation (FM).



**FIGURE 1. CERTIFICATION LABEL FROM SCOTT® MODEL S-105
COMBUSTIBLE GAS AND O₂ INDICATOR**

To ensure personnel safety, only approved instruments can be used onsite and only in atmospheres for which they have been certified. When investigating incidents involving unknown hazards, the monitoring instruments should be rated for use in the most hazardous locations. The following points will assist in selection of equipment that will not contribute to ignition of a hazardous atmosphere:

- The mention of a certifying group in the manufacturer's equipment literature does not guarantee certification.
- Some organizations test and certify instruments for locations different from the NEC classifications. The Mine Safety and Health Administration (MSHA) tests instruments only for use in methane-air atmospheres and in atmospheres containing coal dust.
- In an area designated Division 1, there is a greater probability of generating a hazardous atmosphere than in Division 2. Therefore, the test protocols for Division 1 certification are more stringent than those for Division 2. Thus, a device approved for Division 1 is also permitted for use in Division 2, but not vice versa. For most response work, this means that devices approved for Class 1 (vapors and gases), Division 1 (areas of ignitable concentrations), Groups A, B, C, and D should be chosen whenever possible. At a minimum, an instrument should be approved for use in Division 2 locations.
- There are so many groups, classes, and divisions that it may not be possible to certify an all-inclusive instrument. Therefore, select a certified device based on the chemicals and conditions most likely to be encountered. For example, a device certified for a Class II, Division 1, Group E (combustible metal dust) would offer little protection around a flammable vapor or gas.

Accessories or Options

Many manufacturers offer accessories or options for their instruments. A useful option is an alarm to alert the user that a concentration level has been exceeded. This is a common feature on CGIs and oxygen meters.

A recent addition to instruments are microprocessors/dataloggers. This combination can help the operator calibrate the instrument, store calibration information, make adjustments to the instrument, store readings so that a readout of concentrations at specific locations or times can be made at the end of a monitoring period, and report the data. Some units may even do time-weighted averaging of the concentrations. Some instruments can transfer this information into an external computer for storage and data manipulation.

Other accessories and options include special sample probes, special carrying cases, and the ability to change detectors in an instrument.

DATA QUALITY

The *Characteristics of Air Monitoring Instruments* section discussed instrument characteristics (e.g., accuracy, selectivity, and sensitivity) that affect the quality of the data from the air monitoring instruments. Data quality is a concern and EPA has published a document entitled *Data Quality Objectives for Remedial Response Activities* (U.S. EPA 1987) that discusses how to address this concern.

The data quality objectives (DQOs) basically state that the desired quality of data determines the amount of time and effort needed to produce the result. There are different levels of data quality. **Table 4** illustrates this point. The higher the analytical level, the better the quality of data. However, higher analytical levels usually require more time and money.

CONCLUSION

The desired air monitoring instrument is one that is portable, direct-reading, easy to use, and accurate and precise. The instrument should also respond quickly, be capable of detecting ppb and % concentrations, be inherently safe, identify and give concentrations of all the chemicals and hazards in an atmosphere, and do its job while the operator is sitting at a safe distance from the hazardous material site or spill. Unfortunately, no instrument meets these criteria. Thus, a variety of instruments are needed depending on the air monitoring plan.

When preparing an air monitoring plan, the operator must determine why, how, when, and where the monitoring is to be done and what equipment is necessary. In addition, there are legal requirements to comply with. Guidance documents are available to assist in complying with these requirements. Other factors must also be considered when selecting the monitoring equipment. Additional information on why to sample, or what to sample for, will be covered in the *Exposure Limits and Action Levels* section of the course. Characteristics of the various types of equipment will also be discussed in later sections.

TABLE 4. SUMMARY OF ANALYTICAL LEVELS APPROPRIATE TO DATA USES

DATA USES	ANALYTICAL LEVEL	TYPE OF ANALYSIS	LIMITATIONS	DATA QUALITY
SITE CHARACTERIZATION MONITORING DURING IMPLEMENTATION	LEVEL I	<ul style="list-style-type: none"> - TOTAL ORGANIC/INORGANIC VAPOR DETECTION USING PORTABLE INSTRUMENTS - FIELD TEST KITS 	<ul style="list-style-type: none"> - INSTRUMENTS RESPOND TO NATURALLY OCCURRING COMPOUNDS 	<ul style="list-style-type: none"> - IF INSTRUMENTS CALIBRATED AND DATA INTERPRETED CORRECTLY, CAN PROVIDE INDICATION OF CONTAMINATION
SITE CHARACTERIZATION EVALUATION OF ALTERNATIVES ENGINEERING DESIGN MONITORING DURING IMPLEMENTATION	LEVEL II	<ul style="list-style-type: none"> - VARIETY OF ORGANICS BY GC; INORGANICS BY AA; XRF - TENTATIVE ID, ANALYTE-SPECIFIC - DETECTION LIMITS VARY FROM LOW ppm TO LOW ppb 	<ul style="list-style-type: none"> - TENTATIVE ID - TECHNIQUES/INSTRUMENTS LIMITED MOSTLY TO VOLATILES, METALS 	<ul style="list-style-type: none"> - DEPENDENT ON QA/QC STEPS EMPLOYED - DATA TYPICALLY REPORTED IN CONCENTRATION RANGES
RISK ASSESSMENT PRP DETERMINATION SITE CHARACTERIZATION EVALUATION OF ALTERNATIVES ENGINEERING DESIGN MONITORING DURING IMPLEMENTATION	LEVEL III	<ul style="list-style-type: none"> - ORGANICS/INORGANICS USING EPA PROCEDURES OTHER THAN CLP CAN BE ANALYTE-SPECIFIC - RCRA CHARACTERISTIC TESTS 	<ul style="list-style-type: none"> - TENTATIVE ID IN SOME CASES - CAN PROVIDE DATA OF SAME QUALITY AS LEVELS IV, NS 	<ul style="list-style-type: none"> - SIMILAR DETECTION LIMITS TO CLP - LESS RIGOROUS QA/QC
RISK ASSESSMENT PRP DETERMINATION EVALUATION OF ALTERNATIVES ENGINEERING DESIGN	LEVEL IV	<ul style="list-style-type: none"> - HSL ORGANICS/INORGANICS BY GC/MS; AA; ICP - LOW ppb DETECTION LIMIT 	<ul style="list-style-type: none"> - TENTATIVE IDENTIFICATION OF NON-HSL PARAMETERS - SOME TIME MAY BE REQUIRED FOR VALIDATION OF PACKAGES 	<ul style="list-style-type: none"> - GOAL IS DATA OF KNOWN QUALITY - RIGOROUS QA/QC
RISK ASSESSMENT PRP DETERMINATION	LEVEL V	<ul style="list-style-type: none"> - NONCONVENTIONAL PARAMETERS - METHOD-SPECIFIC DETECTION LIMITS - MODIFICATION OF EXISTING METHODS - APPENDIX B PARAMETERS 	<ul style="list-style-type: none"> - MAY REQUIRE METHOD DEVELOPMENT/MODIFICATION - MECHANISM TO OBTAIN SERVICES REQUIRES SPECIAL LEAD TIME 	<ul style="list-style-type: none"> - METHOD-SPECIFIC

Source: U.S. EPA. 1987. *Data Quality Objectives for Remedial Response Activities*. EPA/540/G-87/003. U.S. Environmental Protection Agency.

EXPOSURE LIMITS AND ACTION LEVELS

PERFORMANCE OBJECTIVES

At the end of this lesson, participants will be able to:

- Identify the three sources of exposure limits specified in OSHA's 29 CFR 1910.120 *Hazardous Waste Operations and Emergency Response* standard
- Define the terms "time-weighted average (TWA) limit," "short-term exposure limit," and "ceiling limit"
- Given the identity and concentration of a chemical exposure, determine whether an exposure limit is exceeded
- Calculate an 8-hour TWA exposure when given a chemical's exposure concentration and the duration of the exposure
- List the three uses mentioned in 1910.120 for exposure limits
- List three of the five applications for which the American Conference of Governmental Industrial Hygienists states the threshold limit values should not be used
- List EPA's action levels for oxygen, combustible gas, and radiation and the actions associated with each level.

NOTES

EXPOSURE LIMITS AND ACTION LEVELS

EXPOSURE LIMITS (29 CFR Part 1910.120)

- Permissible Exposure Limits (PELs)
 - 29 CFR Part 1910, Subparts G and Z, Occupational Safety and Health Administration (OSHA)

EXPOSURE LIMITS (29 CFR Part 1910.120)

- Published Exposure Levels
 - *NIOSH Recommendations for Occupational Health Standards*, 1986
 - American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs) and Biological Exposure Indices (BEIs) for 1987-1988

NOTES

EXPOSURE LIMITS Sources

- OSHA
 - PELs
 - Legal requirements
 - 1968 TLVs and American National Standards Institute (ANSI)
 - 29 CFR 1910.1000 (tables)
 - Specific standards - benzene

EXPOSURE LIMITS Sources

- National Institute for Occupational Safety and Health (NIOSH)
 - Recommended exposure limits (RELs)
 - May be legal (1910.120)
 - Rationale in criteria documents
 - Immediately dangerous to life or health (IDLH)

EXPOSURE LIMITS Sources

- ACGIH
 - TLVs
 - Recommendations
 - May be legal (1910.120)
 - Yearly booklet
 - Documentation

NOTES

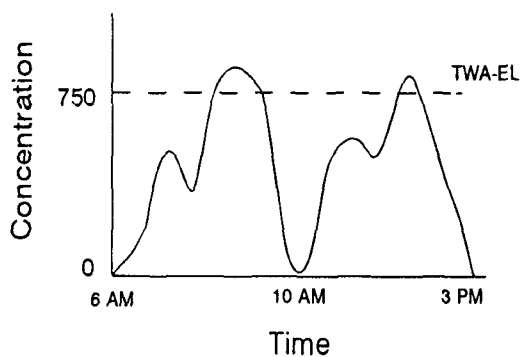
EXPOSURE GUIDELINES Sources

- American Industrial Hygiene Association (AIHA)
 - Workplace environmental exposure levels (WEELs)
 - Recommendations
 - Yearly updates
 - Documentation

EXPOSURE GUIDELINES Sources

- Other
 - U.S. Army and U.S. Air Force
 - Mine Safety and Health Administration (MSHA)
 - Other countries (e.g., Federal Republic of Germany maximum concentration values in the workplace (MAKs))

TIME-WEIGHTED AVERAGE (TWA)



NOTES

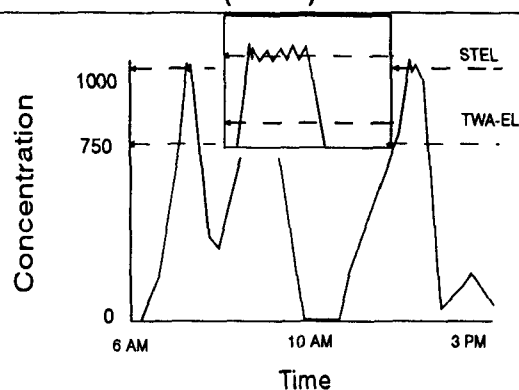
TIME-WEIGHTED AVERAGE CALCULATION

Exposures: 1500 ppm for 1 hour
500 ppm for 3 hours
200 ppm for 4 hours

$$\frac{(1 \text{ hr})(1500 \text{ ppm}) + (3 \text{ hrs})(500 \text{ ppm}) + (4 \text{ hrs})(200 \text{ ppm})}{8 \text{ hrs}} =$$

$$\frac{1500 \text{ ppm} + 1500 \text{ ppm} + 800 \text{ ppm}}{8} = 475 \text{ ppm}$$

SHORT-TERM EXPOSURE LIMIT (STEL)

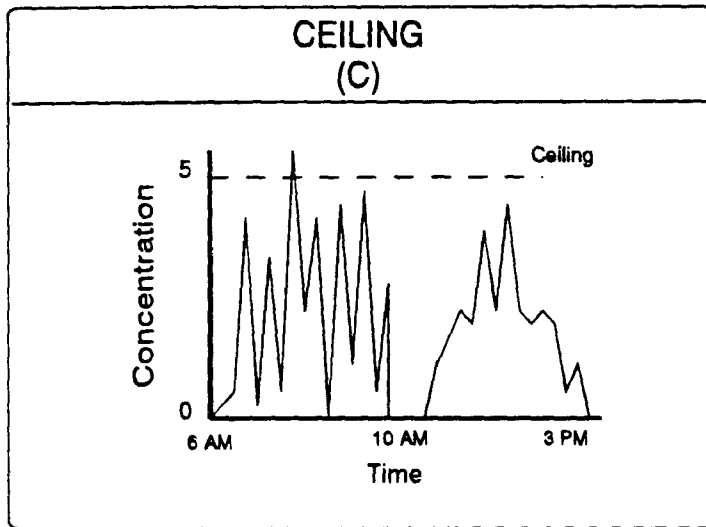


STEL

Excursions to the STEL

- Should not be longer than 15 minutes in duration (OSHA, NIOSH, ACGIH)
- Should be at least 60 minutes apart (ACGIH)
- Should not be repeated more than 4 times per day (ACGIH)
- Supplement TWA

NOTES



CEILING

The exposure that shall not be exceeded during any part of the work day. If instantaneous monitoring is not feasible, the ceiling shall be assessed as a 15-minute TWA exposure (unless otherwise specified) that shall not be exceeded at any time during a work day

Source: NIOSH Recommendations for Occupational Safety and Health. 1992.

COMPARISON OF EXPOSURE LIMITS			
Chemical	OSHA	NIOSH	ACGIH
Acetone	1000*	250	750/1000
Benzene	1/5	0.1/C 1	10 (0.1)
Lead (mg/m ³)	0.05	<0.1	0.15 (0.05)
Benzaldehyde	NA	NA	NA

Note: * units are ppm; TWASTEL
() indicates intended change

NOTES

IDLH

"...means an atmospheric concentration of any toxic, corrosive, or asphyxiant substance that poses an immediate threat to life or would cause irreversible or delayed adverse health effects or would interfere with an individual's ability to escape from a dangerous atmosphere."

Source: 29 CFR 1910.120(a)

IDLH

IDLH concentrations represent the maximum concentration from which, in the event of respirator failure, one could escape within 30 minutes without a respirator and without experiencing any escape-impairing or irreversible health effects.

Note: IDLH level defined by the Standards Completion Program - NIOSH/OSHA - only for purposes of respirator selection

IDLH VALUES Examples

Chemical	IDLH
Acetone	20,000 ppm (LEL?)
Benzene	Ca (3000 ppm)
Lead	700 mg/m ³
Tetraethyl lead	40 mg/m ³
Benzaldehyde	Not available

Source: NIOSH Pocket Guide to Chemical Hazards. 1990.

NOTES

EVALUATION OF A MIXTURE

$$E_m = C_1/L_1 + C_2/L_2 + \dots C_n/L_n$$

E_m = the equivalent exposure for the mixture

C = the concentration of a particular contaminant

L = the exposure limit for that contaminant

EVALUATION OF A MIXTURE Example

Chemical A $C = 500 \text{ ppm}$ $L = 750 \text{ ppm (TWA)}$

Chemical B $C = 200 \text{ ppm}$ $L = 500 \text{ ppm (TWA)}$

Chemical C $C = 50 \text{ ppm}$ $L = 200 \text{ ppm (TWA)}$

$$E_m = (500/750) + (200/500) + (50/200)$$

$$E_m = 0.67 + 0.40 + 0.25$$

$$E_m = 1.3$$

EVALUATION OF A MIXTURE

- E_m should not exceed 1
- The calculation applies to chemicals where the effects are the same and are additive
- Do not mix TWAs, STELs, or ceilings

NOTES

EXPOSURE LIMITS

Used to determine:

- Site characterization
- Medical surveillance
- Exposure controls
 - Engineered controls
 - Work practices
 - Personal protective equipment (PPE)

Source: 29 CFR 1910.120

THRESHOLD LIMIT VALUES

Not intended for use:

- As a relative index of toxicity
- In the evaluation or control of community air pollution nuisances
- In estimating the toxic potential of continuous, uninterrupted exposures or other extended work periods

Source: ACGIH TLVs and BEIs for 1993-1994

THRESHOLD LIMIT VALUES

Not intended for use:

- As proof or disproof of an existing disease or condition
- For adoption by countries whose working conditions differ from those in the United States of America and where substances and processes differ

Source: ACGIH TLVs and BEIs for 1993-1994

NOTES

ENVIRONMENTAL EXPOSURE LIMITS

- U.S. EPA
 - National Ambient Air Quality Standards Program (NAAQS)
- State/Local
 - NAAQS
 - Modified TLVs
 - Risk assessment

ACTION GUIDE

- The chemical concentration or instrument reading at which a specific action should be taken
- Sources:
 - EPA Standard Operating Safety Guides (SOSGs)
 - OSHA standards for specific chemicals may require an action (e.g., medical monitoring) if one-half the PEL is reached (action level)

EPA ACTION GUIDES Combustible Gas Indicator

Level	Action
<10% LEL (<5%)*	Continue monitoring with caution
10-25% LEL	Continue monitoring, but with extreme caution
>25% LEL (>5%)*	Explosion hazard! Withdraw from area immediately.

* Confined space

NOTES

EPA ACTION GUIDES Oxygen Concentration

Level	Action
<19.5%	Monitor wearing SCBA.
19.5-25%	Continue monitoring with caution. SCBA not needed based only on oxygen content.
>25%	Discontinue monitoring. Fire potential! Consult specialist.

EXPOSURE LIMITS AND ACTION LEVELS

INTRODUCTION

It is necessary, for response activities involving hazardous materials, to acknowledge and plan that response personnel may become exposed. Most hazardous materials have levels of exposure that can be tolerated without adverse health effects. However, it is imperative to determine:

- The identity of materials involved
- The type and extent of exposure
- The possible health effects from overexposure
- The exposure limits and/or action levels considered safe for each hazardous material encountered.

SOURCES FOR EXPOSURE LIMITS FOR AIRBORNE CONTAMINANTS

Several organizations have proposed exposure limits for chemicals and other hazards. The Occupational Safety and Health Administration (OSHA) is one such organization. It is charged with protecting the health and safety of workers. In 29 CFR 1910.120, the *Hazardous Waste Operations and Emergency Response* standard, OSHA specifies the use of certain exposure limits. The exposure limits that are specified are OSHA's permissible exposure limits (PELs) and "published exposure levels." The published exposure levels are used when no PEL exists. A published exposure level is defined as:

the exposure limits published in "NIOSH Recommendations for Occupational Health Standards" dated 1986 incorporated by reference. If none is specified, the exposure limits published in the standards specified by the American Conference of Governmental Industrial Hygienists in their publication "Threshold Limit Values and Biological Exposure Indices for 1987-88" dated 1987 incorporated by reference. (29 CFR 1910.120 (a)(3))

Organizations that have developed exposure limits are discussed below. Not all of these groups are specifically mentioned in 1910.120. Many of the following organizations have exposure guidelines for exposures to hazards other than airborne contaminants (e.g. heat stress, noise, radiation). This part will deal only with airborne chemical exposures.

Occupational Safety and Health Administration

In 1971, the OSHA promulgated PELs. These limits were extracted from the 1968 American Conference of Governmental Industrial Hygienists' (ACGIH) threshold limit values (TLVs), the American National Standards Institute (ANSI) standards, and other federal standards. The PELs are found in 29 CFR 1910.1000. Since then, additional PELs have been adopted and a few of the

originals have been changed. These initial changes have been incorporated into specific standards for chemicals (e.g., 29 CFR 1910.1028 - benzene). There are also standards for 13 carcinogens for which there is no allowable inhalation exposure.

OSHA is a regulatory agency. Therefore, its PELs are legally enforceable standards and apply to all private industries and federal agencies. Depending on state or local laws, the PELs may also apply to state and local employees.

National Institute for Occupational Safety and Health

NIOSH was formed at the same time as OSHA. NIOSH conducts scientific research and recommends occupational safety and health standards. The exposure levels NIOSH has researched have been used to develop new OSHA standards. However, many recommended exposure limits (RELs) have not been adopted by OSHA. Unless OSHA adopts NIOSH RELs into a standard (like 1910.120), they are only recommendations. The RELs are found in the *NIOSH Recommendations for Occupational Health Standards*.

NIOSH also publishes criteria documents that provide information on handling specific chemicals. These documents also provide rationale for the chemical's exposure limit. Additionally, NIOSH publishes immediately dangerous to life or health (IDLH) values in its *Pocket Guide to Chemical Hazards*. IDLHs will be discussed later.

American Conference of Governmental Industrial Hygienists

One of the first groups to develop exposure limits was ACGIH. In 1941, ACGIH suggested the development of maximum allowable concentrations (MACs) for use by industry. A list of MACs was compiled by ACGIH and published in 1946. In the early 1960s, ACGIH revised those recommendations and renamed them TLVs.

"Threshold Limit Values (TLVs) refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects." (*Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*, ACGIH). The publication further states that the TLVs "are developed as guidelines to assist in the control of health hazards. These recommendations or guidelines are intended for use in the practice of industrial hygiene, to be interpreted and applied only by a person trained in this discipline." (Policy Statement on the Uses of TLVs and BEIs).

Along with the TLVs, ACGIH publishes biological exposure indices (BEIs). BEIs are to be used as guides for evaluation of exposure where inhalation is not the only possible route of exposure. Because the TLVs are for inhalation only, they may not be protective if the chemical is ingested or absorbed through the skin. Biological monitoring (e.g., urine samples and breath analysis) can be used to assess the overall exposure. This procedure uses information about what occurs in the body (e.g., metabolism of benzene to phenol) to determine if there has been an unsafe exposure. The BEIs serve as a reference for biological monitoring just as TLVs serve as a reference for air monitoring.

The TLVs are reviewed yearly and are published in ACGIH's *Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*.

American Industrial Hygiene Association (AIHA)

The AIHA has provided guidance for industrial hygienists for many years. In 1984, AIHA developed exposure guidelines that it calls Workplace Environmental Exposure Level Guides (WEELs®). These are reviewed and updated each year. Although the list is not as large as others, AIHA has chosen chemicals for which other groups have not developed exposure limits. Thus, they are providing information to fill the gaps in information sources.

Other Organizations

In the United States, the Army and Air Force have also developed exposure limits for their purposes. The Mine Safety and Health Administration (MSHA) has health standards for air contaminants that may be encountered during mining activities.

Other countries have also developed exposure limits. An example are the Federal Republic of Germany's maximum concentrations at the workplace (MAKs). They can be found in ACGIH's *Guide to Occupational Exposure Values* along with PELs, RELs, and TLVs.

Even though the other organizations are not part of the list of published exposure limits in 1910.120, they are sources that may be useful. 1910.120 (g) suggests looking at published literature and material safety data sheets (MSDS) if PELs or published exposure limits do not exist.

TYPES OF EXPOSURE GUIDELINES

Although there are different organizations that develop exposure guidelines, the types of guidelines they produce are similar.

Time-Weighted Average (TWA)

A TWA exposure limit is the average concentration of a chemical most workers can be exposed to during a 40-hour work week and a normal 8-hour work day without showing any toxic effects. Some TWA exposure limits (e.g., NIOSH) can also be used to evaluate exposures up to 10 hours. The TWA permits exposure to concentrations above the limit, provided these excursions are compensated by equivalent exposure below the TWA. **Figure 1** shows an example that illustrates this point for a chemical (e.g., acetone) with a TWA exposure limit of 750 ppm.

A TWA exposure is determined by averaging the concentrations during the different exposure periods over an 8-hour period with each concentration weighted based on the duration of exposure. For example, an exposure to acetone at the following concentrations and durations would have an 8-hour TWA exposure of:

- 1500 ppm for 1 hour
- 500 ppm for 3 hours
- 200 ppm for 4 hours

$$\frac{(1 \text{ hr})(1500 \text{ ppm}) + (3 \text{ hrs})(500 \text{ ppm}) + (4 \text{ hrs})(200 \text{ ppm})}{8 \text{ hrs}} =$$

$$\frac{1500 \text{ ppm} + 1500 \text{ ppm} + 800 \text{ ppm}}{8} = 475 \text{ ppm}$$

This exposure would be compared to an 8-hour TWA exposure limit.

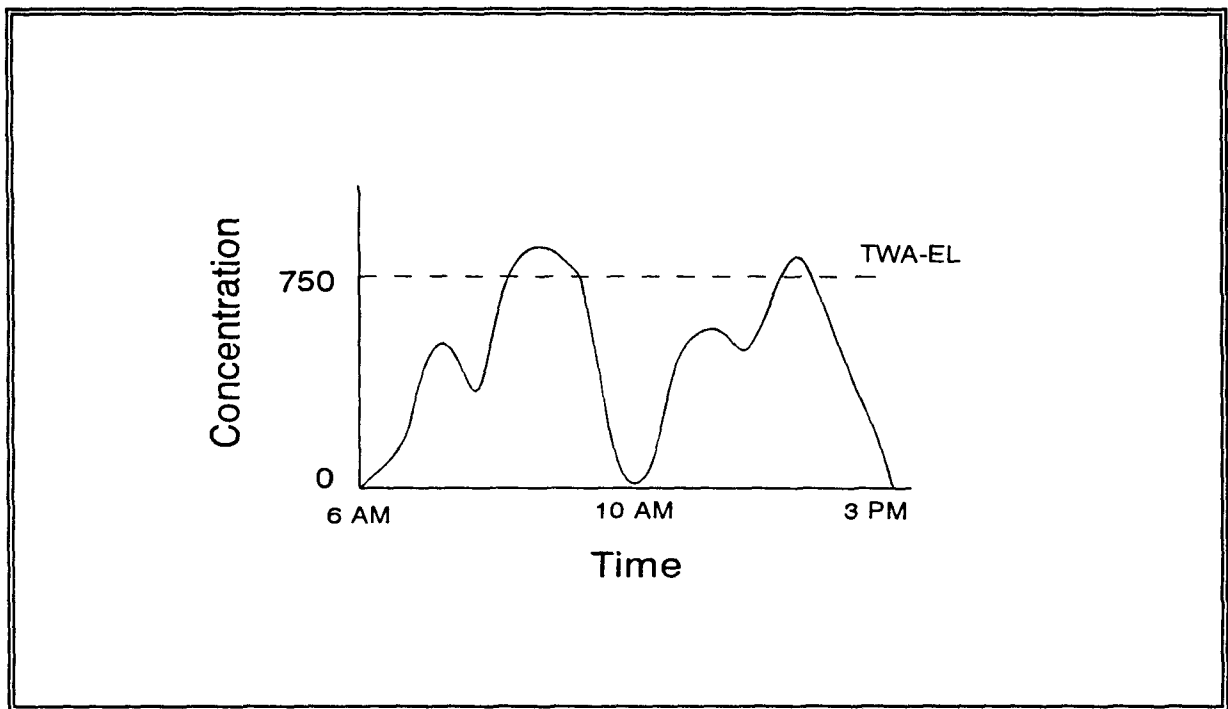


FIGURE 1. EXAMPLE OF AN EXPOSURE COMPARED TO A TWA EXPOSURE LIMIT

Short-Term Exposure Limit (STEL)

The excursions allowed by the TWA exposure could involve very high concentrations. This might cause an adverse effect but still be within the allowable average. Therefore, some organizations felt there was a need to limit these excursions. OSHA, NIOSH, and ACGIH define the STEL as a 15-minute TWA exposure limit. ACGIH has the additional stipulation that excursions to the STEL should not be longer than 15 minutes in duration, should be at least 60 minutes apart, and should not be repeated more than 4 times per day. **Figure 2** illustrates an exposure that does not exceed the

15-minute limit for an STEL of 1000 ppm (note that in the previous example of an 8-hour TWA calculation, the acetone STEL was exceeded but the TWA was not).

The STEL supplements the TWA and does not replace it. Both exposure limits should be used. The STEL reflects an exposure limit protecting against acute effects from a substance which primarily exhibits chronic toxic effects. This concentration is set at a level to protect workers against irritation, narcosis, and irreversible tissue damage.

AIHA has some short-term TWAs that are similar to the STELs. The times used vary from 1 to 30 minutes. These short-term TWAs are used in conjunction with, or in place of, the 8-hour TWA. There is no limitation on the number of these excursions or the rest period between each excursion.

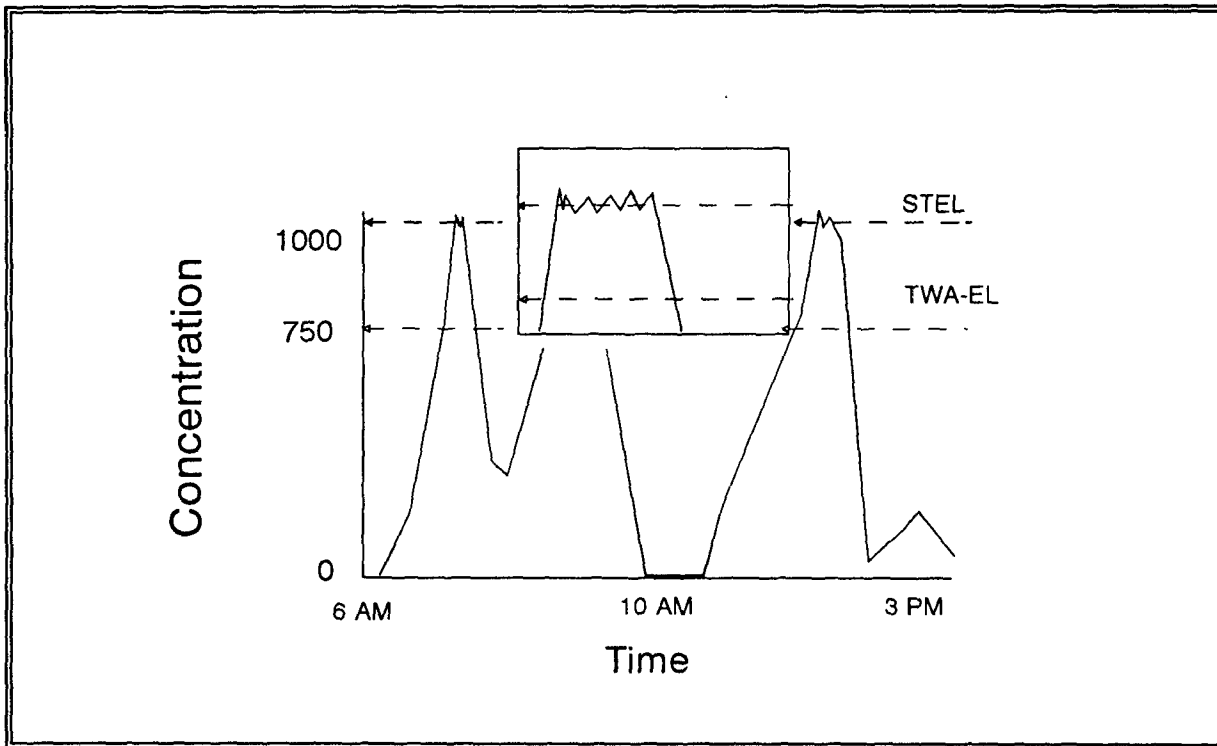


FIGURE 2. EXAMPLE OF AN EXPOSURE COMPARED TO AN STEL AND A TWA

Ceiling (C)

Ceiling values exist for substances for which exposure could result in a rapid and specific response. The ceiling is that concentration that should not be exceeded during any part of the work day. If instantaneous monitoring is not feasible, the ceiling shall be assessed as a 15-minute TWA exposure (unless otherwise specified) that shall not be exceeded at any time during a work day. A ceiling value is denoted by a "C" preceding the exposure limit.

Figure 3 illustrates an exposure that exceeds a ceiling value of 5 ppm.

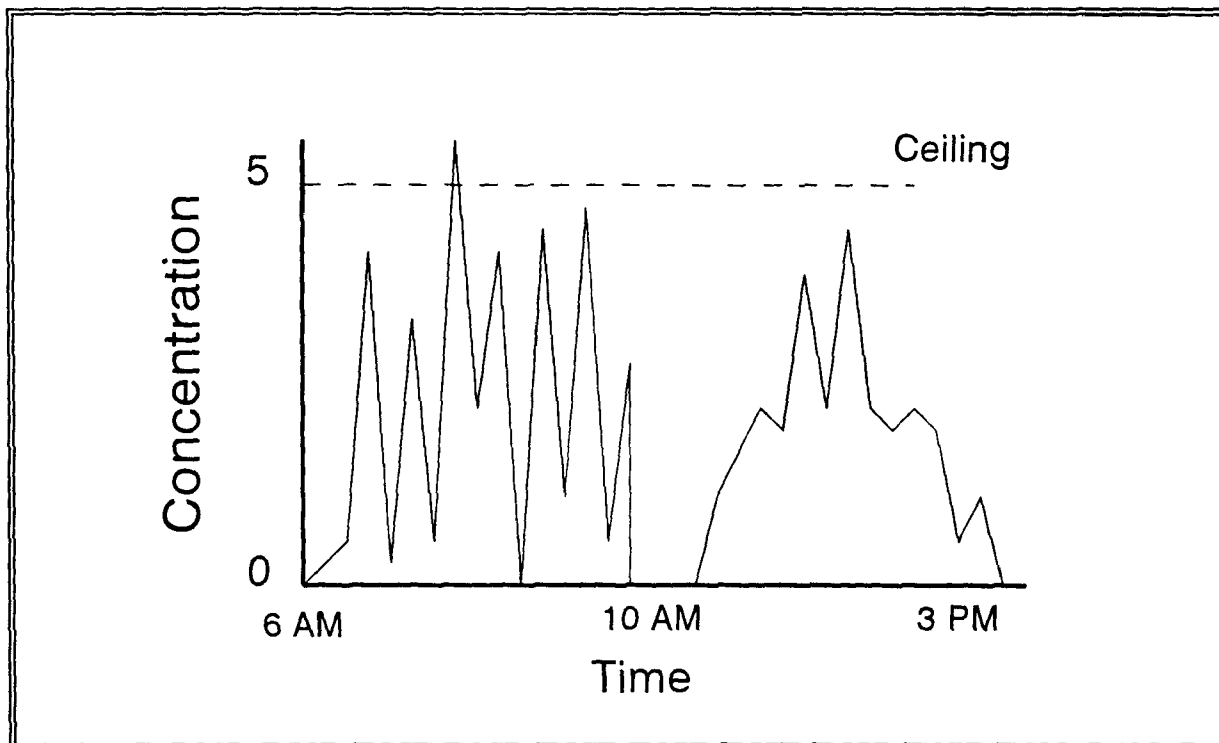


FIGURE 3. EXAMPLE OF AN EXPOSURE COMPARED TO A CEILING EXPOSURE LIMIT

Peaks

"Acceptable maximum peak" concentrations can be found in OSHA's 1910.1000 Table Z-2. Table Z-2 contains exposure limits that OSHA had adopted from ANSI. This peak exposure is an allowable excursion above the ceiling values for the chemicals. The duration and number of exposures at this peak value is limited. For example, for those industries not incorporated in 1910.1028, OSHA allows the 25-ppm ceiling value for benzene to be exceeded to 50 ppm, but only for 10 minutes during an 8-hour period.

Skin Notation

Whereas these exposure guidelines are based on exposure to airborne concentrations of chemicals, the organizations recognize that there are other routes of exposure in the workplace. In particular, there can be a contribution to the overall exposure from skin contact with chemicals that can be absorbed through the skin. Unfortunately, there are few data available that quantify the amount of allowable skin contact.

Some organizations provide qualitative information about skin-absorbable chemicals. When a chemical has the potential to contribute to the overall exposure by direct contact with the skin, mucous membranes, or eyes, it is given a "skin" notation.

This skin notation not only points out chemicals that are readily absorbed through the skin, but also notes that if there is skin contact, the exposure limit for inhalation may not provide adequate

protection. The inhalation exposure limit is designed for exposures only from inhalation. If additional routes of exposure are added, there can be detrimental effects even if the inhalation exposure limit is not exceeded.

Immediately Dangerous to Life or Health (IDLH)

As defined in the NIOSH *Pocket Guide to Chemical Hazards*, "IDLH concentrations represent the maximum concentration from which, in the event of respirator failure, one could escape within 30 minutes without a respirator and without experiencing any escape-impairing or irreversible health effects." Although 30 minutes is stated in the definition, this is not a 30 minute allowable exposure limit. NIOSH's purpose in developing this IDLH was for respirator selection.

Other organizations, such as ANSI, OSHA, and MSHA, have similar definitions for IDLH, but not always the same application. It is accepted by all of these groups that IDLH conditions include 1) toxic concentrations of contaminants, 2) oxygen-deficient atmospheres, and 3) explosive, or near-explosive (above, at, or near the lower explosive limits), environments.

Guidelines for potentially explosive, oxygen-deficient, or radioactive environments can be found in the EPA's *Standard Operating Safety Guides* and the NIOSH/OSHA/USCG/EPA publication entitled *Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities*.

At hazardous material incidents, IDLH concentrations should be assumed to represent concentrations above which only workers wearing respirators that provide the maximum protection (i.e., a positive-pressure, full-facepiece, self-contained breathing apparatus [SCBA] or a combination positive-pressure, full-facepiece, supplied-air respirator with positive-pressure escape SCBA) are permitted. Specific IDLH concentration values for many substances can be found in the NIOSH *Pocket Guide to Chemical Hazards*. For some chemicals, NIOSH gives a "Ca" designation along with a concentration for IDLH. Ca denotes those chemicals that NIOSH considers to be potential human carcinogens. NIOSH recommends the highest level of respiratory protection for exposure to these substances, even below IDLH. However, carcinogenic effects were not considered when developing the IDLH concentrations.

MIXTURES

The exposure limits that have been discussed are based on exposure to single chemicals. Because many exposures include more than one chemical, values are adjusted to account for the combination. When the effects of the exposure are considered to be additive, a formula can be used to determine whether total exposure exceeds the limits. The following calculation is used:

$$E_m = (C_1 \div L_1) + (C_2 \div L_2) + \dots (C_n \div L_n)$$

where:

- E_m = the equivalent exposure for the mixture
- C = the concentration of a particular contaminant
- L = the exposure limit for that substance.

The value of E_m should not exceed unity (1).

An example using this calculation would be as follows:

Chemical A	C = 500 ppm; L = 750 ppm (TWA)
Chemical B	C = 200 ppm; L = 500 ppm (TWA)
Chemical C	C = 50 ppm; L = 200 ppm (TWA)

$$\begin{aligned}E_m &= (500 \div 750) + (200 \div 500) + (50 \div 200) \\E_m &= 0.67 + 0.40 + 0.25 \\E_m &= 1.3\end{aligned}$$

Because E_m exceeds unity, the exposure combination may be a problem. The next step should be to determine whether exposure limits are based on similar effects. This calculation applies to chemicals where the effects are the same and are additive. If the combination is not additive, the calculation is not appropriate. Also, mixing TWA, STEL, and ceiling limits in this equation is not appropriate.

APPLICATION OF EXPOSURE GUIDELINES

OSHA's *Hazardous Waste Operations and Emergency Response* standard specifies uses for exposure limits.

Site Characterization

29 CFR 1910.120 (c) (3) requires identification of IDLH conditions during site characterization. 29 CFR 1910.120 (h) (3) requires air monitoring upon initial entry to identify IDLH conditions, other dangerous conditions, and exposures over the exposure limits.

Medical Surveillance

29 CFR 1910.120 (f) (2) (i) requires a medical surveillance program for all employees exposed to substances or hazards above the PEL for 30 or more days per year. If there is no PEL, then the published exposure levels are used for evaluation. The exposures are considered even if a respirator was being used at the time of exposure.

Exposure Controls

Engineered Controls and Work Practices

29 CFR 1910.120 (g) (1) (i) states "Engineering controls and work practices shall be instituted to reduce and maintain employee exposure to or below the permissible exposure limits for substances regulated by 29 CFR Part 1910, to the extent required by Subpart Z, except to the extent that such

controls and practices are not feasible." [emphasis added] Whenever engineering controls and work practices are not feasible, personal protective equipment shall be used to reduce and maintain exposures.

For those substances or hazards where there is no PEL, the published exposure levels are used. If there are no PELs or published exposure limits, published literature and MSDS may be used for evaluation. In these circumstances, a combination of engineering controls, work practices, and personal protective equipment (PPE) shall be used to reduce and maintain exposures.

Personal Protective Equipment

Because the selection of PPE must be based on the hazards present at the site, the exposure limits are used to evaluate the appropriate PPE. Comparing the actual or expected exposure to the PEL or other exposure limits gives the wearer information on selection of the proper PPE.

LIMITATIONS AND RESTRICTIONS OF USE

The exposure guidelines discussed in this section are based on industrial experience, experimental human studies, experimental animal studies, or a combination of the three. The guidelines were developed for workers in the industrial environment. Thus, they are not meant to be used for other purposes. ACGIH in its *Threshold Limit Values and Biological Exposure Indices* states:

These limits are intended for use in the practice of industrial hygiene as guidelines or recommendations in the control of potential health hazards and for no other use, e.g., in the evaluation or control of community air pollution nuisances; in estimating the toxic potential of continuous, uninterrupted exposures or other extended work periods; as proof or disproof of an existing disease or physical condition; or adoption by countries whose working conditions differ from those in the United States of America and where substances and processes differ. These limits *are not* fine lines between safe and dangerous concentration nor are they a relative index of toxicity. They *should not* be used by anyone untrained in the discipline of industrial hygiene.

As can be seen from this qualifier, these exposure limits are not intended as exposure limits for exposure to the public.

There is the limitation on the use of the exposure guideline as a relative index of toxicity. This is because the exposure limits are based on different effects for different chemicals. For example, the TLV-TWA for acetone is chosen to prevent irritation to the eyes and respiratory system. The TLV-TWA for acrylonitrile is chosen to reduce the risk to cancer. Exposures to these chemicals at other concentration levels could lead to other effects. Thus, when evaluating the risk of chemical exposure, consult the documentation for the exposure limit along with other toxicological data.

NON-OCCUPATIONAL EXPOSURE LIMITS

As mentioned earlier, the occupational exposure limits are not intended for use in evaluating public health hazards. However, they are often used because there may not be anything else available. In other situations, a group may feel that the exposure may be for a short duration and the occupational exposure limits are adequate. For example, many computer air dispersion models for emergency response use the TLVs as action levels.

Some agencies have applied modifiers to the occupational exposure limits to adjust them for public health use. These modifiers may include adjustments for exposure time (168 hours for the public compared to 40 hours for occupational situations) and safety factors for sensitive populations (dividing the exposure limit by 10). While groups like ACGIH discourage this application of their data, the users argue that modification of human data is preferred to extrapolation of animal data.

In some cases, ambient air quality standards or guidelines have been developed for application to public exposure. The federal government and many states have developed them. They are based on modification of occupational exposure limits, risk assessment data, or both. EPA has developed national ambient air quality standards in response to the Clean Air Act. The current list is very limited and only some chemicals (e.g., lead and particulates) are applicable to waste sites.

In the risk assessment approach for chemical exposure, it is recognized that the public exposure to a chemical may involve more than one route of exposure. With this approach, it is not appropriate to use just an inhalation exposure limit. Results from air sampling are combined with other sample results (e.g., drinking water and soil) to determine total exposure and risk.

ACTION LEVELS

Action levels can be developed for specific chemicals, hazards, or situations. The concept of an action level is that if the action level is not exceeded, then there is little probability that a hazardous exposure will occur.

In some of its specific standards, OSHA uses an action level that is one-half of the PEL. For example, the action level for benzene is 0.5 ppm calculated as an 8-hour TWA. If this level is exceeded, continual air monitoring and medical surveillance can be required.

EPA in its *Standard Operating Safety Guides* gives actions to take if certain instrument readings (levels) are obtained during monitoring. These are listed in **Table 1**.

In some situations, site-specific action levels for direct-reading instruments may be developed. This is done by using knowledge about what chemicals are present on the site and the instrument's response to the chemicals. Whereas this may not be as accurate as using special monitoring equipment and laboratory analysis, it allows rapid response to a potentially hazardous situation.

CONCLUSION

There are many sources for exposure limits and action levels. Some of these are legal requirements; some are guidelines. The goal is to use these numbers to protect personnel working with hazardous materials.

TABLE 1. ATMOSPHERIC HAZARD ACTION GUIDES

Monitoring Equipment	Atmospheric Hazard ^a	Level	Action
Combustible gas indicator	Explosive	< 10% LEL	Continue monitoring with caution.
		10–25% LEL	Continue monitoring, but with extreme caution, especially as higher levels are encountered.
		≥ 25% LEL	Explosion hazard! Withdraw from area immediately.
Oxygen concentration		< 19.5%	Monitor wearing SCBA. <i>Note:</i> Combustible gas readings not valid in atmospheres with less than 19.5% oxygen.
		19.5–25%	Continue monitoring with caution. SCBA not needed based <u>only</u> on oxygen content.
		> 25%	Discontinue monitoring. Fire potential! Consult specialist.
Radiation survey instrument	Gamma radiation	Above background:	
		< 1 mR/hr	Continue monitoring. Consult a Health Physicist.
		≥ 1 mR/hr	Withdraw. Continue monitoring only upon the advice of a Health Physicist.
Colorimetric tubes	Organic and inorganic vapors/gases	Depends on chemical	Consult reference manuals for air concentration vs. PEL/TLV and toxicity data.
Photoionization detector	Organic vapors/gases	Depends on chemical	Consult reference manuals for air concentration vs. PEL/TLV and toxicity data.
Flame ionization detector	Organic vapors/gases	Depends on chemical	Consult reference manuals for air concentration vs. PEL/TLV and toxicity data.

^a Hazard classes are general and not all compounds in these classes can be measured by realtime instruments.

Note: The correct interpretation of any instrument readout is difficult. If the instrument operator is uncertain of the significance of a reading, especially if conditions could be unsafe, a technical specialist should immediately be consulted. Consideration should be given to withdrawing personnel from the area until approval by the safety officer is given to continue operations.

3. Role of Audit Team Members

3.1 Audit Team Composition

An EPA audit team consists primarily of EPA employees, and other designated representatives, including contractors and the American Association of Retired Persons (AARP) enrollees. The participation of other federal, state, and local government personnel, particularly SERC and LEPC representatives, is encouraged, but they should be made aware that they will be entering and accessing information from a facility under their own authorities. Section 3.3 of this Manual further discusses the participation of non-EPA audit team personnel.

The audit team can vary in size, depending upon the level of detail of the audit (e.g., number of chemicals and/or processes under investigation; national significance). At a minimum, however, there must be two technical experts on a team for collection and verification of technical findings and observations. **[Required Activity]**

The following list represents suggested roles, responsibilities, associated disciplinary backgrounds, and other parameters for composing a team. This list is provided as guidance and in no way is a required format for forming an audit team. In many cases, your team composition may require you to combine or divide roles.

Team Leader

- Must be EPA employee; **[Required Activity]**
- Coordinates audit logistics, makes team assignments, coordinates initial liaison with facility personnel, and coordinates preparation and distribution of final site visit report; and
- Provides any needed follow-up information.

Deputy Team Leader

- Must be EPA employee or designated representative; **[Required Activity]**
- Provides logistical support, as directed by Team Leader; and
- Assumes other responsibilities delegated by Team Leader.

Chemical Process Hazards Reviewer

- Must be EPA employee or designated representative;
- Responsible for collection and verification of process-related information;

- Primary liaison with facility technical personnel; and
- Requires technical knowledge of chemical hazards, process engineering, and maintenance procedures.

Chemical Accident Prevention Reviewer

- Must be EPA employee or designated representative;
- Responsible for collection and verification of facility information;
- Liaison with appropriate facility technical personnel;
- Requires technical knowledge of chemical accident prevention, including hazard evaluation and modeling techniques and release prevention/mitigation systems.

Safety and Training Reviewer

- Must be EPA employee or designated representative;
- Responsible for collection and verification of facility information;
- Primary liaison with facility health and safety personnel;
- Requires knowledge of operator, safety, and worker right-to-know training programs.

Emergency Planning and Response Reviewer

- Must be EPA employee or designated representative;
- Responsible for collection and verification of facility information;
- Primary liaison with appropriate facility personnel responsible for planning and response;
- Requires knowledge of emergency planning and response requirements.

Technical expertise for the chemical safety audit program refers to knowledge, experience, and disciplinary training in plant process design, engineering, operations, training, and emergency planning. Example disciplines include:

- Chemical, civil, industrial/safety, and environmental engineering,
- Plant process experience,
- Environmental science,

- Industrial hygiene,
- Geology, and
- Environmental and emergency management and planning.

Personnel with the appropriate expertise can be found in the following regional program offices: media (e.g., air, water, radiation); RCRA; TSCA; Superfund (e.g., emergency preparedness and response, removal, health, and safety); and Research and Development.

In selecting team members, the skill base of the team must accommodate the need for coverage of the major audit elements:

- Process and safety system technologies;
- Operating procedures;
- Training programs;
- Emergency planning activities; and
- Management activities.

Specific tasks should be assigned to each team member. Each member should know his/her respective role in all facets of the facility audit. Certain members may be assigned the lead on one or more facets of the audit, and the other team members, because of their individual skills and experiences, should be prepared to contribute to the completion of that facet of the audit.

In summary, an EPA audit team can consist of EPA employees, EPA contractors (e.g., Technical Assistance Team), AARP enrollees, and representatives from federal, state, and local governments. Two basic restrictions apply to the "team;" one, the Team Leader must be an EPA employee, and two, the Chemical Process Hazards Reviewer must be an EPA employee or designated representative (i.e., EPA employee, contractor, or AARP enrollee). [**Required Activity**] This last restriction is required to ensure continuity in communicating the audit scope and intent.

The following provides an overview of the anticipated roles and responsibilities for EPA employees, contractors/TAT personnel, and AARP enrollees:

- EPA employees coordinate audit program and lead the audit team.
- Contractors/TAT personnel provide technical support as defined by EPA.
- AARP enrollees:
 - Provide support role in audits;
 - Apply professional expertise and experience in chemical engineering or other technical or industrial fields for reviewing process safety technologies at facilities;

- Apply other expertise in such areas as safety management or training for involvement in other aspects of the audit (i.e., reviewing emergency plans, training manuals, and emergency notification procedures and/or systems);
- Participate in report preparation, including observations and recommendations from the audit;
- Identify facilities for potential audits, using information sources such as Accidental Release Information Program (ARIP) data, and coordinate with regional response centers; and
- Are limited to field activities that do not stress physical limitations.

3.2 Training and Safety Requirements

Field activities for EPA employees are subject to the training requirements embodied in EPA Order 1440.2, Health and Safety Requirements for Employees Engaged in Field Activities. The Order establishes policies, responsibilities, and mandatory requirements for occupational health and safety training and certification, and occupational medical monitoring.

EPA Order 1440.2 requires that a Site Safety Plan be developed for EPA employees conducting a chemical safety audit at a facility handling hazardous substances. EPA regional offices can either use the model site safety plan (see **Attachment 3**), or develop their own program that complies with EPA Order 1440 and the Occupational Safety and Health Administration's worker protection standards codified at 29 CFR 1910 and 1926. The plan should include a description of the proposed audit scope, facility health hazards, necessary protective equipment, contractor participation, and decontamination procedures, and must be completed and approved by the EPA project coordinator, branch chief, on-scene supervisor, and health and safety manager. Under certain circumstances, a more extensive plan may also be required. For more information, contact the safety and health office in your region.

Audit team members should dress appropriately, including steel-toed boots, safety glasses, and hard hats. Team members should provide their own safety equipment, and should not rely on the facility.

Prior to participating in an audit, all EPA team members, which include EPA employees, contractors, and AARP enrollees, must have completed the following training courses:

- Training in occupational health and safety procedures under EPA Order 1440.2. Attending a 24-hour or 40-hour health and safety course that is approved and sponsored by EPA and conducted by EPA or its contracted agents fulfills the requirement of this Order; **[Required Activity]** and
- EPA Chemical Safety Audit Training Course. (Course attendance flexibility is discussed below.)

In addition to the listed training, annual medical monitoring is required. **[Required Activity]**

In some audits, a specialized technical expert (i.e., contractor or other EPA program personnel) who normally does not participate in CSA program activities will assist in conducting the audit. Under these circumstances, it will be difficult for such an individual to have taken the EPA CSA course. Consequently, the requirement for the CSA course is flexible depending upon the situation. The health and safety training requirements and medical monitoring, however, are not flexible. **[Required Activity]** This requirement should not pose any problems, since it would be rare for a technically qualified contractor or EPA employee not to have had this training.

Suggested topics for additional, but not required, training include:

- Handling of confidential business information;
- Interviewing techniques;
- Hazard evaluation techniques;
- Chemical processing techniques;
- Negotiating techniques; and
- Technical writing.

3.3 Non-EPA Personnel Participation on Audit Team

Non-EPA team members may include representatives of other federal agencies and departments, states/SERCs, local officials/LEPCs, and any other group not previously identified as an EPA team member. The regions are encouraged to invite participation by non-EPA personnel in audits, but entry into the facility must be authorized pursuant to authorities other than CERCLA. Participation of non-EPA personnel must be in a support role as defined by the Team Leader. In addition, non-EPA personnel cannot serve in the capacity of Team Leader or Chemical Process Hazards Reviewer. **[Required Activity]**

SERC and LEPC participation is encouraged to enhance their knowledge of chemical hazards and process safety for use in planning activities under SARA Title III and in future Clean Air Act Amendments Risk Management Program activities. SERCs, LEPCs, and other federal agencies also serve as a valuable source of information in preparing for the audit.

It is important to inform these representatives of the required health and safety training that EPA employees and representatives undergo prior to audit participation. As discussed in the next section, non-EPA participants require their own liability coverage.

3.4 Liability

Liability associated with conducting audits is described in the following sections for each group potentially represented on an audit team.

3.4.1 Federal Employees

Under the Federal Employees Liability Reform and Tort Compensation Act of 1988, a suit can no longer be maintained against a Federal employee in his or her individual capacity for any act (discretionary or non-discretionary) performed within the scope of the employee's employment. All such suits must now be brought against the United States government. If named in a suit in his or her individual capacity, employees should promptly notify the Office of Regional Counsel and the Office of General Counsel.

The legislation does not change the potential liability of a Federal employee in his or her individual capacity for grossly negligent actions (usually taking the action out from under the scope of the employee's employment), for Constitutional violations, and for a violation of a statute "for which a claim is otherwise authorized." All audit participants should have audit responsibilities clearly delineated in their job description.

3.4.2 AARP Enrollees

There are no provisions for indemnifying AARP enrollees from personal liability under the cooperative agreement between AARP and EPA. Since AARP enrollees serve only in support roles in all aspects of CSA program implementation, the Regional Chemical Emergency Preparedness and Prevention Coordinators and their staff are responsible for ensuring that enrollees are not placed in situations that could result in job-related personal liability.

3.4.3 Technical Assistance Team Contractors

The Federal Employees Liability Reform and Tort Compensation Act of 1988 only covers TAT contractors when responding to a CERCLA hazardous substance release or performing a clean-up/removal related to such release. Audit activities for TAT contractors are not covered under this Act, since the contractor is not specifically handling hazardous substances, pollutants, or contaminants. TAT contractors must investigate liability coverage with their respective employer.

3.4.4 Federal, State/SERC, and Local/LEPC Government Personnel

All non-EPA personnel will be entering a facility under their own authorities and would require their own liability coverage.

3.5 **Conflict of Interest**

Conflict of interest refers to any person (i.e., EPA employee, contractor, AARP enrollee, non-EPA personnel) who has a financial interest associated with the facility being audited, has been previously employed with the facility, or a facility subsidiary, and/or has been a consultant for the facility. Persons with conflict of interest should not participate in any activities, either on-site or off-site, associated with the facility audit. **[Required Activity]** In addition, such persons must identify themselves to the Team Leader and excuse themselves from the audit of that facility. **[Required Activity]**

4. Preparing for the Audit

4.1 Facility Selection

At present, there are no established procedures for selecting a facility for an audit. Each region has flexibility in identifying facilities. A variety of options useful to identifying a facility are discussed below. Although there is substantial flexibility in facility selection, there are two important requirements:

- A release of a CERCLA hazardous substance, pollutant, or contaminant must have occurred, or there must be "reason to believe" that a threat of such a release exists at the facility; **[Required Activity]** and
- The Office of Regional Counsel and the SERC of the state where the audited facility is located must be consulted to identify any legal actions currently being pursued or anticipated. **[Required Activity]** It is advised that regional media programs also be consulted.

The following list provides a variety of options to consider when selecting a facility. Information sources to be used in evaluating these options include federal, state, and local release notification reports and follow-up reports, OSC reports, Regional Response Centers, ARIP, ERNS, and other sources (see **Attachment 4** and chart in section 4.3).

- Previous release history of the facility;
- SERC and/or LEPC referral;
- Proximity to sensitive population(s);
- Public sensitivity;
- Opportunity for sharing new technology;
- Population density; and
- Concentration of industry in the area.

In addition, the region may wish to select facilities for a chemical safety audit as part of a larger regional initiative, such as an evaluation of facilities using a specific chemical or located near a particularly sensitive environment. For example, during fiscal year 1992 a number of facilities that produce and use hydrogen fluoride were examined by audit teams nationally, while Region 5 conducted all of its audits in coordination with its Great Lakes Basin pollution prevention initiative.

4.2 Facility Notification

Once a facility has been selected, the process of notifying the facility and scheduling the audit can be initiated. Although each region will invariably establish its own procedures for notifying a facility and coordinating the audit, the following suggestions and tools should be integrated into that process. These suggestions are designed to help establish a constructive rapport with the facility and to ensure the correct use of statutory authorities and other legal requirements.

The Team Leader should make an initial phone call to the facility owner/operator. The purpose of this call is to identify a "contact" at the facility for all correspondences, to communicate/explain the purpose and intent of the audit, and to schedule dates for conducting the audit. In some instances, it may be useful to schedule a pre-audit meeting with the facility to obtain further information.

The phone call should be followed by a letter to the facility contact that summarizes the initial conversation and confirms any decisions made during the call. In addition, the letter serves to confirm audit statutory authority, provide the facility an opportunity to claim confidential information, and to identify the contractor, if a contractor is participating. As previously stated in section 2.2.3 of this Manual, the contractor must be identified by contractor name and contract number in order to have access to confidential information.

Attachment 5 is a sample letter designed to fulfill the above goals. While language may be added to the letter, such as a summary of a phone conversation, the legal aspects of the letter as contained in the attachment should not be materially altered. **[Required Activity]** It is suggested that all correspondence with the facility be reviewed by the Office of Regional Counsel (ORC).

Unfortunately, not all efforts to schedule and coordinate an audit based upon the voluntary consent of the facility will be successful. After receiving either the facility's written or verbal denial of EPA's request to conduct the audit, a letter must be sent to the facility (1) confirming this denial; and (2) invoking use of the CERCLA 104(b) and 104(e) authorities for entry. **[Required Activity]** **Attachment 6** contains a sample letter specifically designed for this situation. Preparation of this letter must be coordinated with your Office of Regional Counsel. **[Required Activity]** The suggested letter states that continued refusal of facility access can result in EPA issuing an order requesting entry and/or initiating an enforcement action. Any further activities and contact with the facility should be pursued in coordination with the Office of Regional Counsel.

4.3 Facility Background Information

Preliminary preparation is an important factor in conducting an organized audit. The team may find it useful to collect the facility background information several weeks in advance of the audit. This will require contact with the facility and state and local officials to arrange delivery of these materials. The audit team can then review this information and become more familiar with the facility prior to the audit. Using this technique, the team will be able to prepare a detailed list of topics and questions to help organize their activities during the facility visit. The following list is a sampling of the types and sources of information that will assist a team in preparing for the audit:

Type of Information	Sources of Information
Release History	OSC reports; ARIP questionnaires; ERNS; SARA Title III sections 304 and 305(b) reports; state release files
Regulatory History	Local, state, and federal air, water, and waste permits; SARA Title III sections 302, 304, 311, 312, and 313 submissions
Hazardous Chemicals (Hazards, Amounts, and Locations)	SARA Title III sections 311 and 312 submissions; OSHA hazard communication and process safety management standard documents; hazards analysis; NIOSH Pocket Guide to Chemical Hazards
Chemical Processes	Industry standards and processing techniques from trade and professional groups (e.g., AIChE, ASSE, and the Chlorine Institute); process flow diagrams and piping and instrumentation diagrams
Community Involvement	CAER; LEPC; and SERC

The "Audit Protocol/Report Preparation Guidance" as presented in section 6.0 of this Manual provides further detail on the types of information that may be requested from the facility prior to conducting the audit. **Attachment 4** contains further information on these listed sources.

4.4 Preparing for the Site Visit

Prior to conducting the on-site audit, a pre-visit meeting should be conducted with the entire audit team, including any non-EPA personnel who will be visiting the facility. This meeting should be held as close to the date of the site visit as possible to keep the important points being emphasized fresh in everyone's mind. By this time, the audit team should already be operating as a unit; all team members should be familiar with the audit protocol, the information previously collected by the team should have been

reviewed, additional information to be obtained at the facility should have been identified, and the team members should have developed individual agendas. The pre-visit meeting serves to reinforce what already is in place and should cover the following items:

- Clearly establish the responsibility and authority of the team leader;
- Review highlights of the audit's objectives and note any specific team member responsibilities;
- Review any personal health and safety issues that may be present at the site for the team to prepare for and avoid (see section 3.2);
- Review information about key personnel and operations at the site;
- Establish objectives and an agenda for each day of the site visit;
- Cover logistical matters such as a nightly team meeting to discuss results and plan the next day's activity; and
- Cover any other topics that the Team Leader identifies.

5. Conducting the Audit

The on-site chemical safety audit will consist of the following four phases:

- Entry;
- Opening Meeting;
- On-site Activities; and
- Exit Briefing.

5.1 Entry

The audit team should arrive at the facility during normal working hours at a time and date pre-determined with the facility. At the facility entrance office, the facility may provide a blank sign-in sheet, log, or visitor register. It is acceptable for the audit team members to sign it. EPA employees and authorized representatives, however, must not sign any type of "waiver" or "visitor release" which would relieve the facility of responsibility for injury, or which would limit the rights of the Agency to use the data obtained from the facility. **[Required Activity]** When such a waiver or release is presented, the Team Leader should politely explain that such a document cannot be signed, and a blank sign-in sheet should be requested. If the team is refused entry because they do not sign such a release, the Team Leader must report all pertinent facts to the ORC, and leave the facility if the matter cannot be resolved. **[Required Activity]** All events surrounding the refused entry must be fully documented including the name of the person(s) refusing entry. **[Required Activity]** Procedures described in section 4.2 of this Manual concerning refusal of entry must then be followed. **[Required Activity]**

5.2 Opening Meeting

The entire audit team will meet with the plant manager and his/her key staff, and will likely discuss the entire audit. The staff of the plant manager could include superintendents of safety and operations, a lawyer, and corporate representation. The team should be very clear about its purpose and should be prepared to discuss the audit starting with an explanation of the CSA program, facility selection, the audit purpose and scope, the background research performed, the specific objectives for the site visit, and the report that will be written.

During the meeting, the audit team should outline its specific on-site agenda and the cooperation needed to accomplish that agenda. In addition, the meeting provides a good opportunity for the facility to provide the audit team with an overview of its

operations and safety programs and may include a general tour of the whole facility (as appropriate). This meeting typically requires at least a half day.

5.3 On-Site Activities

Once past the opening meeting, the audit team may split up into smaller groups to take a plant tour and interview other operations and management personnel. The plant tour should include specific tours of the chemical handling and process areas. The team should interview personnel involved in such areas as process safety, process operations, technical support, personnel, emergency planning and response, and environmental management.

During these tours and interviews, individual team members should be obtaining information and making observations that fulfill the needs of their individual responsibilities. The questions and prompts for discussion contained in the annotated audit protocol can be helpful.

During this or any other part of the site visit, it is possible that an observation will be made or that information will be obtained that should be of significance to the audit team, but that is beyond the scope of the facility audit. In this event, the Team Leader should be notified.

5.4 Exit Briefing

In this final meeting, the entire audit team will meet with the plant manager and his/her key staff to discuss the results of the audit as it presently stands. The plant manager may be accompanied by the same people who attended the opening meeting. The facility will want to know about all significant team findings and, more importantly, about the conclusions that have been drawn and the recommendations that will be made.

Prior to the exit briefing, the audit team should have a private meeting to establish an agenda for this meeting. Significant observations and findings should be listed for discussion with the facility. The team should identify conclusions based on this information only to the extent that a consensus among team members can be reached. A team consensus is also necessary for identifying any recommendations to the facility at this time. In the absence of team consensus, it is inappropriate to offer conclusions or recommendations to the facility during the exit briefing. This does not, however, preclude drawing such conclusions or making any recommendations in the audit report that will be written later.

6. Audit Protocol/Report Preparation Guidance

6.1 Purpose and Structure

This protocol/report preparation guidance (see **Exhibits 1 and 2**) provides a detailed topic outline to direct the scope and content of the audit and a structure for preparation of the audit report. The protocol and report format have been integrated to accomplish the following goals:

- Provide detailed guidance on the types of information that should be reviewed during the audit and discussed in the report;
- Ensure continuity in report preparation; and
- Provide an organized and detailed report format for easy access to specific lessons learned on chemical process safety management practices.

Because of the scope of the audit or the resources and expertise of the audit team, it may not need, or be able, to address all areas of the protocol. However, all areas of the protocol should be addressed in the audit report (e.g., state that the audit team did not review the facility's hazard evaluation and modeling capabilities).

By providing this Manual to facility personnel prior to conducting the audit, the facility will also have a more thorough understanding of the audit scope and intent. The facility can prepare for the audit by assembling information and identifying personnel with the required expertise to assist the audit team.

This guidance is structured to address each of the major elements of chemical process safety management at the facility being audited. These include:

- Facility Background Information;
- Chemical Hazards;
- Process Hazard Information;
- Chemical Accident Prevention;
- Accidental Release/Incident Investigation;
- Facility Emergency Preparedness and Planning Activities;
- Community Emergency Planning and Response Activities; and
- Public Alert and Notification Procedures.

Preceding each of these sections in the annotated protocol/report guidance (**Exhibit 2**) is a brief overview of the purpose of this section with respect to the audit scope.

Exhibit 1

Outline of Protocol/Report Preparation Guidance

- 1.0 INTRODUCTION
- 2.0 SUMMARY OF FINDINGS/CONCLUSIONS
- 3.0 BACKGROUND
 - 3.1 General Facility and Audit Information
 - 3.2 Purpose of the Audit and Facility Selection Process
 - 3.3 Audit Methodology
- 4.0 FACILITY BACKGROUND INFORMATION
 - 4.1 Site and Surrounding Area Description
 - 4.1.1 Facility Profile
 - 4.1.2 Site Topography and Meteorological Conditions
 - 4.1.3 Site Access
 - 4.1.4 Special/Sensitive Populations and Environments
 - 4.1.5 Regional Demographics
 - 4.1.6 Identification of Vulnerable Zones
- 5.0 CHEMICAL HAZARDS
 - 5.1 Overview of Hazards for Chemical(s) Being Audited
 - 5.2 Facility Management of Chemical Hazard Data
- 6.0 PROCESS INFORMATION FOR HAZARDOUS CHEMICALS
 - 6.1 Storage and Handling
 - 6.1.1 Storage Systems
 - 6.1.2 Shipping/Receiving
 - 6.1.3 Material Transfer
 - 6.2 Process Description
 - 6.2.1 Overview of Processing Steps and Operating Procedures
 - 6.2.2 General Description of Process Equipment Capacity
 - 6.2.3 Back-ups and Redundancy
 - 6.2.4 Process Parameter Monitoring
 - 6.2.5 Environmental Monitoring

6.3 Process Hazards

7.0 CHEMICAL ACCIDENT PREVENTION

7.1 Management Activities

7.1.1 Corporate Role in Facility Process Safety Management

7.1.2 Facility Role in Process Safety Management

7.1.3 Audit Activities and Procedures

7.2 Process Operation and Maintenance

7.2.1 Standard Operating Procedures

7.2.2 Training Practices

7.2.3 Equipment Maintenance Procedures

7.2.4 Instrument Maintenance

7.3 Hazard Evaluation and Modeling

7.3.1 Hazard Evaluation

7.3.2 Modeling

7.4 Release Prevention Systems

7.5 Mitigation Systems

8.0 ACCIDENT RELEASE INCIDENT INVESTIGATION

8.1 History of Accidental Releases/Incidents

8.2 Facility Investigation Procedures

9.0 FACILITY EMERGENCY PREPAREDNESS AND PLANNING ACTIVITIES

9.1 Facility Emergency Response Plan

9.2 Emergency Response Exercises and Simulations

9.3 Fire, Evacuation, and Rescue Corridors

9.4 Emergency Equipment Provisions

9.5 Emergency Response Chain of Authority

9.6 Emergency Response Management Procedures

9.7 Emergency Communication Network within the Facility

9.8 Emergency Response Personnel Training Requirements

9.9 Follow-up Release Procedures

10.0 COMMUNITY AND FACILITY EMERGENCY RESPONSE PLANNING
ACTIVITIES

- 10.1 Facility Planning and Outreach Activities with Community
- 10.2 Local/Community Emergency Response Planning

11.0 PUBLIC ALERT AND NOTIFICATION PROCEDURES

- 11.1 Procedures for Public Notification of Releases
- 11.2 Schedule for Testing Procedures
- 11.3 History of Notification Procedures and Evaluation
- 11.4 Community and Facility Contacts
- 11.5 Facility and Media Interaction

12.0 CONCLUSIONS

13.0 RECOMMENDATIONS

APPENDICES

Exhibit 2

Annotated Protocol/Report Preparation Guidance

STANDARD DISCLAIMER (see **Attachment 7**)

1.0 INTRODUCTION

- Purpose and scope of the audit program (**Attachment 8** contains standard language to describe the purpose and scope of the program); and
- Paragraphs identifying facility name and location and why audited

2.0 SUMMARY OF FINDINGS/CONCLUSIONS

- Briefly summarize audit findings (both positive and negative)

3.0 BACKGROUND

3.1 GENERAL FACILITY AND AUDIT INFORMATION

- Facility name, location, principal activities;
- Dates audit conducted; and
- Listing of team members and their affiliation, areas of responsibility, and expertise.

3.2 PURPOSE OF THE AUDIT AND FACILITY SELECTION PROCESS

- Briefly explain why facility was selected. Audit could be conducted for a number of reasons such as:
 - To follow up on an accidental release or series of releases (include description of triggering incident);
 - To focus on particular technologies, processes, operations, or chemicals;
 - Regional or headquarters initiatives;
 - At request of state and/or local officials; or
 - At facility invitation.

3.3 AUDIT METHODOLOGY

- Summary of the process areas and other locations that were investigated and why they were selected; and
- Important audit limitations (e.g., no comparison of safety systems across several similar operations was performed).

4.0 FACILITY BACKGROUND INFORMATION

A history of site activities and a description of the surrounding area provides information on the potential risk that facility activities may pose to the surrounding community and the environment in the event of an accidental chemical release.

4.1 SITE AND SURROUNDING AREA DESCRIPTION

4.1.1 Facility Profile

- Facility history and principal activities (i.e., date built, modifications and improvements, releases, etc.), size and layout, and ancillary operations (e.g., power generation, warehouse, distribution center, laboratory, waste treatment, etc.); and
- Reference maps in appendix or use simple maps in text.

4.1.2 Site Topography and Meteorological Conditions

- Natural disaster potential (e.g., earthquake, flood);
- Geology; and
- Climate.

4.1.3 Site Access

- Transportation routes, including railroad and waterways; and
- Site security (e.g., fencing and gates, security guards, and access by non-authorized persons).

4.1.4 Special/Sensitive Populations and Environments

- Hospitals, schools, and nursing homes; and
- Wetlands, drinking water supply, etc.

4.1.5 Regional Demographics

- Economy, population, industrial and growth patterns

4.1.6 Identification of Vulnerable Zones

5.0 CHEMICAL HAZARDS

This section serves to not only focus briefly on the hazards associated with particular substances, but to provide pertinent facts on the facility's understanding of what are the chemical hazards for each substance.

5.1 OVERVIEW OF HAZARDS FOR CHEMICAL(S) BEING AUDITED

- Brief description of hazards; and
- Reference detailed information in appendix (i.e., MSDS, etc.) -- do not rewrite MSDS information.

5.2 FACILITY MANAGEMENT OF CHEMICAL HAZARD DATA

- What the facility recognizes as the hazards associated with the chemical(s);
- Documentation available on hazards associated with chemical(s) (e.g., MSDS, corrosion rates, reactivity data, etc.);
- Availability of such data to employees (e.g., OSHA Hazard Communication Standard training);
- Mechanism for reviewing and updating information;
- Mechanism for documenting suspected acute and chronic toxic effects (e.g., medical and industrial hygiene personnel); and
- On-site availability of emergency medical care.

6.0 PROCESS INFORMATION FOR HAZARDOUS CHEMICALS

A review of facility operations associated with the processing of the chemical(s) being examined can reveal facility practices and techniques for handling process hazards, as well as reveal facility understanding of the process hazards. (Within each subsection, the report should address every chemical and process examined during the audit for which observations, conclusions, and/or recommendations were noted.)

6.1 STORAGE AND HANDLING

6.1.1 Storage Systems

- Storage methods;
- Capacity;
- Location, including compatibility and spacing;
- Hazard identification (placards and labelling);
- Maintenance and housekeeping of area; and
- Block diagrams to illustrate major process flows.

6.1.2 Shipping/Receiving

- Method(s) of receiving and shipping (e.g., tank trucks, rail cars, pipelines, cylinders, barges, etc.);
- Schedules and quantities of shipments;
- Responsible personnel and level of training;
- Coordination of transportation issues with the community contingency plan; and
- Transportation corridors used.

6.1.3 Material Transfer

- Transfer method(s) from storage to processing areas and between different stages of process;
- Pipe coding/labelling for flow direction and contents;
- Other transfer systems (e.g., compressors, ejectors, pumps, blowers, etc.);
- Housing of transfer systems; and
- Off-site accessibility.

6.2 PROCESS DESCRIPTION

6.2.1 Overview of Processing Steps and Operating Procedures

- Listing different operations and process steps in chronological order for hazardous chemical; can use block-type flow diagram to illustrate steps;
- Chemical production or use rates;
- Chemical reaction(s) description (e.g., catalysts, activators, inhibitors, exothermic, etc.);
- Blending or separation steps;
- Material incompatibilities;
- Pressure and temperature variations; and

- Consequences of deviation: what happens to chemicals spilled, leaked, vented, etc.

6.2.2 General Description of Process Equipment

- Capacity and design conditions;
- Construction material;
- Flow rates;
- Parameters monitored, controlled, and recorded (at equipment or in control room);
- Production or use rates for chemical; and
- Comparison of design limits and operating parameters.

Note: **Attachment 9** contains further guidance on reviewing process operations.

6.2.3 Back-ups and Redundancy

- List systems with back-ups or automatic shutdowns;
- Description of back-ups and how and why used;
- Availability of back-up power systems;
- Method of detecting inoperative control equipment and availability of back-ups; and
- For facility with scrubbers or flares, their capacity for handling accidental releases.

6.2.4 Process Parameter Monitoring

- Description of process parameters for operations and processes and why used;
- Performance history at facility;
- Monitoring and recording procedures; and
- Procedures for addressing unsafe parameter levels.

6.2.5 Environmental Monitoring

- Description of system(s) used to monitor hazardous chemical levels within work areas and in the surrounding environment (e.g., types, location, etc.);
- Connection to alarm and communication systems; and
- Performance history at facility.

6.3 PROCESS HAZARDS

- Hazards facility has identified for the process and determined to present a significant risk to the facility and/or the surrounding community (e.g., storage tank failure, pipeline leak, process vessel overpressurization)

7.0 CHEMICAL ACCIDENT PREVENTION

Practices and technological systems for controlling the process hazards presented in section 6.0 of this protocol/report outline, are an important part of chemical process safety management. This section is intended to describe mechanisms for implementing and maintaining safe process systems. Management directives are reviewed in this section to identify goals and implemented activities, such as training and equipment maintenance procedures, that present the facility's perspective and commitment to safe management of process hazards.

7.1 MANAGEMENT ACTIVITIES

7.1.1 Corporate Role in Facility Process Safety Management

- Corporate safety policy, guidance, and directives; and
- Technical and financial assistance (e.g., process modifications, information exchanges, and capital improvements).

7.1.2 Facility Role in Process Safety Management

- Policy and directives;
- Goals and objectives; and
- Employee safety committees and incentive programs.

7.1.3 Audit Activities and Procedures

- Frequency of facility audits;
- Responsible department and involvement of external personnel (e.g., corporate and private consultants);
- Audit scope;
- Audit procedures and time frame; and
- Implementation of audit recommendations (e.g., policy and procedures).

7.2 PROCESS OPERATION AND MAINTENANCE

7.2.1 Standard Operating Procedures

- SOP manuals available (e.g., operating procedures manual, supervisory operating manual, safety manual, accident and fire prevention manual);
- How procedures/manuals reviewed and approved;
- Listing of personnel roles and responsibilities;
- Applicability of manuals to tasks conducted during normal and emergency situations;
- Other process guides: operating logs, shift turnover procedures, overtime procedures, call out procedures during emergencies, reporting procedures for unusual circumstances or process deviations;
- Experimental operating conditions for process changes, and management of change; and
- Startup, shutdown, and routine operation checklists.

Note: **Attachment 10** contains a summary of the types of documentation and other materials that the audit team may want to review for more information on facility SOPs.

7.2.2 Training Practices

- Types of training available for operations and maintenance personnel;
- Methods and frequency of training;
- Who performs training and qualifications;
- Frequency and procedures for revising training;
- Refresher courses and retraining;
- Upset simulations and drills;
- Use of process simulators;
- Job duty qualifications/prerequisites;
- Types and frequency of job qualification evaluations (e.g., performance reviews, tests);
- Employee turnover rate; and
- Master qualification list.

7.2.3 Equipment Maintenance Procedures

- Work order systems;
- Maintenance and testing scheduling;
- Preventive and predictive maintenance;
- Equipment history records;
- System for spare parts control;
- Level of training;

- Frequency and method of communication between maintenance and operations personnel;
- Prioritization of maintenance and inspections;
- Securing equipment during shift breaks;
- Assuring proper repairs replacement; and
- Management of change for equipment (e.g., appropriateness of materials of construction).

7.2.4 Instrument Maintenance

- Work order systems;
- Frequency and testing of instrument calibration, sensor inspections, and alarm and interlock inspections;
- Instrument history records;
- System for spare parts control;
- Frequency and method of communication between maintenance and operations personnel;
- Number of employees and shift coverage;
- Level of training;
- Management of change for instruments (e.g., appropriateness of calibration settings); and
- Error checking.

7.3 Hazard Evaluation and Modeling

7.3.1 Hazard Evaluation

- Type(s) or method(s) used at facility (e.g., What If, Hazop, etc.) and why selected;
- Processes and operations evaluated;
- Procedures for targeting/scheduling evaluation (e.g., new procedures, process modification, incidents);
- Frequency and basis for updating methods;
- Who participates in and reviews evaluation(s) and the qualifications of such personnel;
- Use of results and methods of documentation;
- Performance of consequence analysis to understand impacts of any potential release;
- Implementation of results and recommendations; and
- How is process change managed.

7.3.2 Modeling

- Uses and types of models for tracking releases into air, surface water, and groundwater;
- Processes, chemicals, and operations to which models have been applied;
- Goals of modeling activities (e.g. support for emergency planning and emergency response);
- Assumptions built in to the models (both by user and developer) and facility perceptions of strengths and limitations (e.g. dense gas releases, terrain effects, single-phase versus multi-phase modeling capability);
- Parameters covered by surface and groundwater models (e.g. degradation, photolysis, volatilization, geochemical processes, local hydrology, adsorption, desorption);
- Validate model against experimental measurements; and
- Use during incidents and the results (e.g., improvements in emergency response or planning).

7.4 Release Prevention Systems

- Facility activities related to preventing a release
 - Description of type(s) of systems in place;
 - Why used;
 - Performance history at facility;
 - Testing and inspections; and
 - Modifications performed.

Examples of activities to prevent chemical releases:

- Improvements in process and equipment design;
- Reduction of inventories;
- Changes in siting of particular equipment;
- Increased training and safety reviews;
- Improved process controls;
- Installation of interlocks; and
- Failsafe design.

7.5 MITIGATION SYSTEMS

- Description of type(s) of system(s) in place;
- Why used;

- Performance history at facility; and
- Frequency of testing and inspections.

Examples of release mitigation systems include:

- Water sprays and sprinkler systems;
- Foams;
- Physical separation of buildings and equipment; and
- Physical barriers, including dikes, curbing, raised doorways, and containment walls).

8.0 ACCIDENTAL RELEASE INCIDENT INVESTIGATION

Facility procedures for identifying the underlying causes of unplanned incidents, including fires, explosions, or releases of hazardous chemicals, and for preventing similar incidents from recurring serve as an important step toward the actual prevention of future incidents.

8.1 HISTORY OF ACCIDENTAL RELEASES/INCIDENTS

- Types (e.g., reportable, near miss);
- Chronicle of releases;
- Reporting history; and
- Community response and interaction.

8.2 FACILITY INVESTIGATION PROCEDURES

- Written procedures (e.g., guidelines, time frames);
- Types of releases to be investigated (e.g., near misses; or those reportable under federal, state, or local law);
- Personnel responsible for investigations;
- Management involvement;
- Actions taken resulting from investigation; and
- Use of reports to share results (e.g., through training programs and lessons learned) and distribution scheme.

9.0 FACILITY EMERGENCY PREPAREDNESS AND PLANNING ACTIVITIES

Emergency activities in preparing for and responding to accidental releases illustrate facility knowledge, dedication, and practices for mitigating incidents.

9.1 Facility Emergency Response Plan

- Type and coverage of facility response plans (e.g., OSHA emergency action plan, SPCC plan, corporate plan);
- Update schedule and procedures (i.e., how often revised and by whom); and
- Key procedural areas covered (e.g., release notification, evacuation, response and mitigation activities).

9.2 Emergency Response Exercises and Simulations

- Types, frequency, and groups involved; and
- Uses of findings.

9.3 Fire, Evacuation, and Rescue Corridors

- Procedures for conducting evacuations;
- Condition and accessibility of fire and rescue corridors; and
- Detail and location of facility and community maps (Maps should be referenced in appendix.).

9.4 Emergency Equipment Provisions

- Types;
- Locations;
- Inspection and maintenance policies, including testing; and
- Sources of equipment (off-site versus on-site).

9.5 Emergency Response Chain of Authority

- Chain of command (e.g., designation of control during an emergency); and

- Coordination with off-site response personnel.
- 9.6 Emergency Response Management Procedures
 - Management's role in response incident situations.
- 9.7 Emergency Communication Network within the Facility
 - Types and accessibility of communication system(s) and backups, including sirens, walkie-talkies, and phones;
 - Testing of communication system; and
 - Ability of personnel to interpret warning signals.
- 9.8 Emergency Response Personnel Training Requirements
 - Categories of facility emergency response personnel;
 - Type of training available and frequency;
 - Who performs training; and
 - Refresher courses.
- 9.9 Follow-up Release Procedures
 - Incident clean-up (e.g., self, private contractors); and
 - After-action review of response with all involved parties (e.g., public and private organizations).

10.0 COMMUNITY AND FACILITY EMERGENCY RESPONSE PLANNING ACTIVITIES

Communication to the community about facility activities and coordination with the community in developing emergency response plans indicate a level of facility commitment to safety, as well as revealing unique outreach activities.

- 10.1 Facility Planning and Outreach Activities with Community
 - Awareness and participation in LEPC activities;
 - Participation in CAER activities; and

- Outreach activities, scholarship programs, open houses, joint training, education, etc.

10.2 Local/Community Emergency Response Planning

- Community plan status;
- Coordination between facility and community in plan preparation and exercise;
- Coordination with hospitals and emergency medical services on treatment of chemical exposure victims;
- Coordination with community response structures and procedures; and
- Mutual aid efforts and facility involvement in non-facility-related community responses.

11.0 PUBLIC ALERT AND NOTIFICATION PROCEDURES

Public alert and notification procedures identify unique procedures and facility commitment to safety for the community.

11.1 Procedures for Public Notification of Releases

- Alarm systems (e.g. sirens, air horns, whistles);
- Communication networks (e.g., radio, television, phone); and
- Back-up systems.

11.2 Schedule for Testing Procedures

- Frequency of tests; and
- Number and type of individuals notified.

11.3 History of Notification Procedures and Evaluation

- Type of incident;
- Timeliness of public notification; and

- Number of individuals notified and methods of public and private emergency notification.

11.4 Community and Facility Contacts

- Alternate contacts; and
- Telephone number update procedures.

11.5 Facility and Media Interaction

- Direct communication links; and
- History of past interaction.

12.0 CONCLUSIONS

The conclusions highlight safety practices observed at the facility. As described in section 6.2.2, *Tips for Writing the Report*, the information should be presented in a factual manner and should refrain from judgments of adequacy or inadequacy. This section summarizes facility practices that reflect the facility's understanding of and commitment to chemical process safety management.

13.0 RECOMMENDATIONS

If applicable, the audit team may wish to make one or more recommendations regarding observed processes, practices, technologies, and so forth. Any such recommendations should be stated clearly, and be practical and technologically feasible at the facility. Recommendations are not required or mandatory actions that must be taken by the facility. They should be presented as options that the facility may consider to enhance their knowledge of and practices in chemical process safety management.

APPENDICES

During the audit process, the team will gather a variety of materials relating to the operations of the facility. Most of this material, however, while very helpful in conducting the audit and preparing the audit report, does not belong in the main body of the audit report and should instead be placed in appendices or maintained in the files of the regional office for future use. Examples of the types of material that might be included as appendices are:

- Sample facility memoranda, guidelines, SOPs, policy statements;
- Correspondence between the facility and the regional office; and
- Graphics such as photographs, maps, charts.

All materials should be labeled with the:

- Name of the facility;
- Date of the audit; and
- Other necessary identifying information.

6.2 Writing the Report

6.2.1 Post-Visit Meeting

The entire audit team should reassemble as soon as possible after completion of the site visit. This is important because the details of the site visit can become confused and fade rapidly. Certain items should be covered in this meeting:

- Require that team members immediately review and edit their notes from the site visit to obtain clarity and completeness;
- Begin using the audit report outline as a basis for organizing all audit information;
- Consider the major audit elements during the review and analysis process, the initial stage in to the completion of the audit report:
 - Facility Background Information;
 - Chemical Hazards;
 - Process Hazard Information;
 - Chemical Accident Prevention;
 - Accidental Release/Incident Investigation;
 - Facility Emergency Preparedness and Planning Activities;
 - Community and Facility Emergency Response Planning Activities; and
 - Public Alert and Notification.
- Review all important observations and findings identified to this point in the audit; and
- Determine whether or not any particular conclusions can be drawn or recommendations made for inclusion in the report.

6.2.2 Tips for Writing the Report

There are two main areas of consideration when preparing a report:

- Writing style; and
- Report format flexibility

Writing style

In many instances during report preparation, several individuals will be working on separate sections pertaining to his/her role in conducting the audit. Although several different writing styles may be presented in the report, it is very important that they all

have one common element of presentation style -- information is factual, relevant, complete, objective, and clear. The entire report, including the *Conclusions* and *Recommendations* sections, should be presented in a factual manner and refrain from judgments of adequacy or inadequacy.

The *Conclusions* section should highlight facility safety practices observed during the audit, identifying unique facility practices that should be shared as well as areas for improvement. This summary should reflect the facility's understanding of, and commitment to, chemical process safety management, and should refrain from judgments of adequacy or inadequacy. As an example of how to present conclusions, consider the following pair of statements:

Incorrect. "The facility has adequate procedures to investigate and respond to the cause(s) of accidental chemical releases."

Correct. "The facility prepares follow-up reports for accidental releases of hazardous chemicals that occur both on- and off-site. The report addresses the cause of the incident, recommended actions to prevent the release from reoccurring, and a schedule and list of responsible individuals for implementing these actions." [If the facility uses a form for this practice, it could be referenced in an appendix.]

The first statement does not provide any information on the facility's follow-up procedures; in addition, a judgement is made on the procedures, which may or may not be valid. The latter illustrates procedures that the facility takes following an accidental release of hazardous chemicals both on- and off-site. Its style of presentation is factual and provides clear information on what the facility does without commenting on the adequacy or inadequacy of the procedures.

The *Recommendations* section should provide clearly stated suggestions and include the factual basis for each recommendation. The recommendations should be both practically and technologically feasible for the audited facility -- they are neither mandatory nor required, and are simply being presented for consideration by the audit team to the facility to enhance its chemical process safety management. As an example of how to present recommendations, consider the following pair of statements:

Incorrect. "The facility should implement a preventive maintenance program."

Correct. "The facility should evaluate the appropriateness of its use of the periodic maintenance system for maintaining pressure relief valves. This evaluation could include, among other aspects, a review of alternative schemes, such as preventive maintenance and predictive maintenance."

The first statement does not provide any information on the facility's existing maintenance program and it does not specify the particular application for the recommended preventive maintenance. The latter clearly describes the current status of

the element in question and provides alternatives for consideration. In addition, the style of presentation is appropriate for the cooperative nature of the audit program. In both the *Conclusions* and *Recommendations* sections, all statements must address observations that are presented in detail in the main body of the report.

Report format flexibility

The introduction to this section of the Manual addresses the purpose and uses of the report protocol/outline. One important purpose is to ensure consistency in report preparation. This consistency will help to facilitate analysis of conclusions and recommendations and will assist CEPPO in effectively identifying successful and problematic practices and technologies, and in sharing information with the regions, other program offices, other federal agencies, state and local governments, facilities, and other involved parties.

There are 13 major report sections (i.e., 1.0, 2.0, etc.), and when preparing the report, each of these must be addressed. **[Required Activity]** For some facilities, however, information relevant to a major section may not exist, or the audit team may not have been able to examine materials relevant to this element. For example, the facility may not have any system for alerting/warning the public that a release has occurred (section 11.0), or this element may not have been reviewed by the audit team. Rather than skip that section of the report, it should be stated that the facility does not have a public alert/warning system, or that this element was not examined in the audit.

6.2.3 Follow-up Information

With almost any audit, there is usually a need to contact the facility after the site visit has occurred to clarify a point or to obtain more complete information. A chemical safety audit is no different. The preferred way to handle follow-up inquiries is for the Team Leader to designate a person or persons to serve as the contact with the facility; the facility may take a similar approach in making any further responses to EPA. This minimizes the opportunity for miscommunication and lends a credible appearance to the conclusion of the audit.

6.2.4 Standard Report Disclaimer

A standard report disclaimer accompanies all audit reports and is located after the cover page. **[Required Activity]** **Attachment 7** contains a sample disclaimer. The report disclaimer serves to describe the scope and limitations of the audit report contents by identifying the time frame in which the audit was conducted, and by clarifying the facility's role in adopting or implementing any of the report contents.

6.3 Review and Finalization Procedures

In preparing the final audit report, there are two considerations to keep in mind:

- Access of draft report information through the Freedom of Information Act (FOIA); and
- Report inclusion of facility confidential information.

6.3.1 Access of Draft Information

In order to ensure that draft report information is not available to the public through FOIA prior to report finalization, the EPA regional office can designate an EPA official (e.g., Section, Division, or Branch Chief) to approve the report as "final." This procedure is not mandatory, but highly recommended, since this process is cited under the Deliberate Process Privilege Section, exemption 5 of FOIA [5 USC 552(b)5].

Additional actions can be taken to prevent draft information from being accessible under FOIA. For example, all draft materials can be stamped "DRAFT." Draft materials can include the following citation at the bottom of each page or on a cover sheet:

"Pre-decisional Document, Not Disclosable Under FOIA"
" - Do Not Cite or Quote - "

Please note that these actions do not have legislative or regulatory authority, as compared to the finalization process described above.

6.3.2 Facility Confidential Information

Another suggested activity during the report finalization process is submission of the draft report to the facility to identify any confidential information. The facility should be contacted to establish a deadline (e.g., two weeks) to avoid lengthy delays. Any information identified as confidential should be treated as such. Comments on the report that are provided by the facility can, but do not have to be taken into consideration as the report is finalized.

6.4 Report Distribution

When the audit report is final, standard distribution by the Regional Chemical Emergency Preparedness and Prevention (CEPP) Coordinator is required to the following groups and organizations: **[Required Activity]**

- SERC and LEPC in which the facility is located;

- Facility owner/operator;
- Facility CEO;
- EPA Headquarters, Chemical Emergency Preparedness and Prevention Office; and
- Any other federal, state, and local agencies or departments that assisted in conducting the audit.

The region should ensure that at least one unbound copy of the report suitable for photocopying is provided to CEPPO.

The Regional CEPP Coordinators should also consider distributing final audit reports to other EPA offices; other federal, state, and local agencies or departments; and other private and public sector organizations. Sharing the report with regional media offices is encouraged. EPA Headquarters will also circulate copies to interested headquarters media offices, the Prevention Work Group, and other federal programs. Press releases of audit activities (e.g., facility visit, report finalization, etc.) are also discretionary for the Regional CEPP Coordinators and EPA Headquarters CEPPO staff.

To help professionals conducting audits, EPA Headquarters is developing a computerized database that contains profiles of all of the chemical safety audit reports. The profiles are summaries of the audit reports organized in a uniform format consistent with the CSA protocol. The database has search capabilities that allow the user to identify report profiles based on SIC code, specific chemical hazards, etc. The information contained in the database will be useful to the regions for a variety of purposes, such as learning how a particular industry operates (e.g., the types of chemicals and kinds of processes in use and the typical problems encountered), as well as identifying field experts and comparing processes at different facilities for the same chemical. CEPPO will also be able to use the database to assemble and distribute information on chemical process safety management and chemical accident prevention issues and to assess the implementation of the CSA program.

6.5 Preparing the Report Profile

An audit report profile should be submitted to headquarters in conjunction with the submission of the audit report for inclusion into the database. The profile (see **Attachments 11 and 12**) organizes the key information contained in the report, including information on the facility and the audit team as well as report conclusions and recommendations, in a format suitable for direct entry into the CSA database. In addition to providing the basis for the continued development of the CSA database, the profile format can also assist the audit team during the audit process. The profile can serve as a method of organizing issues of interest and assigning areas of responsibility to team members prior to the audit, monitoring the progress of the team during the audit

visit, and organizing the collected information during report writing. The specific information that should be included in the CSA report profile is described in the annotated profile in **Attachment 12**. A hardcopy and an electronic version of the profile should accompany the audit report when it is submitted to EPA headquarters to facilitate entering the profile information into the database.

7. Audit Follow-Up Activities

As a supplement to the chemical safety audit and CSA report preparation, each regional office should establish an audit follow-up program. The follow-up program will support EPA's efforts to evaluate the effectiveness of the CSA program in improving, as well as heightening awareness of the need for, chemical process safety among chemical producers, distributors, and users. In addition, it is hoped that the analysis of audit results will provide a basis for amending the focus and direction of the CSA program to better achieve its stated goals at the regional and headquarters level.

Although the specific nature of the follow-up activities has been left to the discretion of the regional offices, at a minimum the program should be designed to track audited facilities' implementation of CSA report recommendations. This will allow Headquarters to analyze trends in the implementation of CSA recommendations as a function of issue (e.g., employee training or instrument maintenance), level of effort (e.g., fixing a relief valve or replacing a storage tank), and type and size of facility. Within this framework, the regional offices are free to examine other audit issues (e.g., format, relationship with state and local officials) at their own discretion and to communicate with the facility in writing or in person.

Optionally, some of the regions also may wish to develop a method to verify whether the information received from the facility is accurate, to the extent that regional resources permit. This may involve the continued participation of state and/or local officials in the audit process or another facility visit by EPA or Technical Assistance Team members.

7.1 Follow-Up Approaches

Currently, some regional offices have already developed follow-up programs. They have approached the follow-up process from a variety of angles, ranging from mailing worksheets to returning to the facilities for a post-audit review. For example:

- Region 6 conducted a comprehensive follow-up effort in FY 92 in which representatives from the region revisited 14 facilities that had been audited since 1989 to evaluate the implementation of audit team recommendations. Issues studied included the most effective audit format; facility attitudes toward the audit process; the role of facility size in implementing recommendations; and the level of expertise of the audit team. Region 6 used the follow-up information to compile quantitative regional data, which was summarized in charts and graphs to highlight key trends and issues. The data indicated that 68 percent of the 173 recommendations were implemented at the facilities involved in the project, with a notably lower rate for the five facilities with greater than 1,000 employees (56%) and for recommendations that involved changes in process design (40%), and a notably higher rate for compliance-related recommendations (100%)

- Region 8 has sent questionnaires to facilities six and 12 months after the audits to check on the facility's progress in implementing the recommendations of the audit team. The questionnaire lists each of the audit team's recommendation, and the facility indicates its response to the recommendations, including their future plans for implementing the recommendations. For the questionnaires completed by facilities in 1991, the region identified an 80-85 percent response rate for facilities in implementing audit recommendations.

Another possible follow-up option suggested by one regional office is to present audited facilities with an evaluation form at the same time as the final audit report is distributed to the facility.

7.2 Specific Information Required

The follow-up program should begin with the facilities at which an audit has been conducted in fiscal year 1993. Regions also have the option of performing follow-up efforts at facilities audited in previous years. For each audit, the regional office should provide EPA Headquarters with the following information:

- Full name and address of audited facility;
- List of recommendations made by the audit team as organized in the CSA report profile prepared by the region;
- Indication of how each recommendation has been or is planned to be implemented and/or addressed by the facility with the date completed or a schedule for implementation, as appropriate;
- Rationale for any recommendations that have not been implemented and/or addressed by the facility; and
- Audit implementation issues, including:
 - Facility attitude toward chemical safety audit, and
 - Successful and problematic audit practices.

Attachments

Attachment 1

Chemical Safety Audit Program Fact Sheet



FACT SHEET

MARCH 1993

CHEMICAL SAFETY AUDIT PROGRAM

BACKGROUND

The Chemical Safety Audit (CSA) program has evolved from the efforts of the U.S. Environmental Protection Agency (EPA) under the Chemical Accident Prevention (CAP) program. The CAP program emerged from concerns raised by the release of methyl isocyanate at Bhopal, India, and of aldicarb oxime at Institute, West Virginia. Awareness of the critical threat to public safety posed by similar incidents led to an emphasis on preparedness and planning for response to chemical accidents. Simultaneous with the development of preparedness activities by EPA was the passage and implementation of the Emergency Planning and Community Right-to-Know Act -- Title III of the Superfund Amendments and Reauthorization Act (SARA) by Congress in 1986. Because prevention is the most effective form of preparedness, the CAP program promotes an effort to enhance prevention activities. The primary objectives of the CAP program are to identify the causes of accidental releases of hazardous substances and the means to prevent them from occurring, to promote industry initiatives in these areas, and to share activities with the community, industry, and other groups.

Many of the key concerns of the CAP program arise from the SARA Title III section 305(b) study entitled Review of Emergency Systems. As part of the information gathering efforts to prepare this study, EPA personnel conducted a number of facility site visits to learn about chemical process safety management practices. The study covers technologies, techniques, and practices for preventing, detecting, and monitoring releases of extremely hazardous substances, and for alerting the public to such releases. One of the key recommendations resulting from the study was the continuation and expansion of the audit program.

As a follow-up to this national prevention study, EPA has undertaken cooperative initiatives with federal agencies, states, industry groups, professional organizations, and trade associations, as well as environmental groups and academia. These joint efforts will serve to determine and implement a means to share information on release prevention technology and practices, and to enhance the state of practice in the chemical process safety arena.

PROGRAM GOALS

The CSA program is part of this broad initiative and has been designed to accomplish the following chemical accident prevention goals:

- Visit facilities handling hazardous substances to gather information on and learn about safety practices and technologies;
- Heighten awareness of the need for, and promote, chemical safety among facilities handling hazardous substances, as well as in communities where chemicals are located;
- Build cooperation among facilities, EPA, and other authorized parties by coordinating joint audits; and
- Establish a database for the assembly and distribution of chemical process safety management information obtained from the facility audits.

PROGRAM AUTHORITY

The Comprehensive, Environmental Response, Compensation and Liability Act (CERCLA or Superfund) was enacted December 11, 1980, and amended by SARA on October 17, 1986. CERCLA authorizes the federal government to respond where there is a release or a substantial threat of a release into the environment of any hazardous substance, pollutant, or contaminant that may present danger to the public health or welfare or to the environment.

CERCLA Sections 104(b) and 104(e), as amended by SARA in 1986, provide authorities for entering a facility and accessing information to conduct a chemical safety audit by EPA. While CERCLA provides authority for states to use statutory authorities for entry and information gathering, such authorities may only be accessed pursuant to a contract or cooperative agreement with the federal government. Since there is no such arrangement, states, as well as local governments, must use their own authorities for audit participation.

As a matter of EPA policy under the CSA program, all facilities that will receive an audit should have experienced a release of a hazardous substance, pollutant, or contaminant, or there should be reason to believe that there exists a threat of such a release. The audits are intended to be nonconfrontational and positive, such that information on safety practices, techniques, and technologies can be identified and shared between EPA and the facility. Involvement in the CSA program by Local Emergency Planning Committees (LEPCs) and State Emergency Response Commissions (SERCs) formed under SARA Title III is encouraged to enhance the goals of both of these programs. However, as stated above, state and local government participation in the audit, itself, must be performed under state and local authorities.

AUDIT SCOPE

The audit consists of interviews with facility personnel, and on-site review of various aspects of facility operations related to the prevention of accidental chemical releases. Specific topics addressed include:

- Awareness of chemical and process hazards;
- Process characteristics;
- Emergency planning and preparedness;
- Hazard evaluation and release detection techniques;
- Operations and emergency response training;
- Facility/corporate management structure;
- Preventive maintenance and inspection programs; and
- Community notification mechanisms and techniques.

Observations and conclusions from audits are detailed in a report prepared by the audit team. The report identifies and characterizes the strengths of specific Chemical Accident Prevention program areas to allow the elements of particularly effective programs to be recognized. Copies of the report are provided to the facility so that weak and strong program areas may be recognized. The audit is conducted following the Guidance Manual for EPA Chemical Safety Audit Team Members, issued by EPA Headquarters. This guidance contains recommended actions, as well as mandatory procedures that must be followed to ensure the health and safety of program auditors and program integrity. Each member of the audit team should have a copy of the manual, and a copy of the manual is transmitted to the audited facility.

AUDIT TEAM COMPOSITION

An EPA audit team primarily consists of EPA employees, and other designated representatives including contractors and the American Association of Retired Persons (AARP) enrollees. Other federal, state, and local government personnel may also be team members. The audit team can vary in size, depending upon the level of detail of the audit (e.g., number of chemicals and/or processes under investigation; national significance).

FACILITY SELECTION

At present, there are no established procedures for selecting a facility for an audit. Each EPA region has flexibility in identifying facilities. Options to consider in selecting a facility include:

- Previous history of the facility;
- SERC and/or LEPC referral;
- Proximity to sensitive population(s);
- Public sensitivity;
- Regional accident prevention initiatives;
- Opportunity for sharing new technology;
- Population density; and
- Concentration of industry in the area.

REPORT DISTRIBUTION

Standard distribution by EPA regional offices of the audit report will be at a minimum to:

- SERC and LEPC in which the facility is located;
- Facility owner/operator and facility CEO;
- EPA Headquarters; and
- Any other federal, state, and local agencies or departments that assisted in conducting the audit.

Distribution is available to other EPA offices, other federal, state, and local agencies or departments, and other private and public sector organizations.

ACCOMPLISHMENTS

During the first four years of the CSA program, the regions have conducted audits at over 150 facilities in 46 states and Puerto Rico. EPA has analyzed the conclusions and recommendations listed in the audit reports to identify trends within and across industries, processes, and chemicals to assist in the further development of the CSA and CAP programs, particularly in light of the accidental release provisions of section 112(r) of the Clean Air Act. At the same time, follow-up activities performed by several of the regional offices indicate that the majority of the recommendations to improve chemical process safety practices suggested by the audit teams have been implemented or are scheduled to be implemented at audited facilities.

CSA PROGRAM BENEFITS

- Identification of effective, field-proven chemical accident prevention technologies and practices.
- Better understanding of the causes of chemical releases.
- Greater awareness by facilities of chemical safety and understanding of available techniques, and specific suggestions for improved programs.
- Identification of problem areas in industry where more attention is needed.
- Cooperation and coordination of chemical safety programs with other federal and state agencies through joint audits and training.

For more information on the Chemical Safety Audit program, contact the Chemical Emergency Preparedness Program (CEPP) office in your EPA regional office.

Attachment 2

CERCLA Provisions Overview and CERCLA Statute

Section 104(a) Removal and Other Remedial Actions

This section provides the federal government with the authority to respond to releases or threatened releases of hazardous substances, pollutants, or contaminants in certain situations.

Section 104(a) authorizes the EPA Administrator "to act, consistent with the national contingency plan, to remove or arrange for the removal of, and provide for remedial action relating to such hazardous substances, pollutants, or contaminants at any time, or take any other response measure consistent with the national contingency plan which the Administrator deems necessary to protect public health or welfare or the environment," where:

- Any hazardous substance is released;
- There is a substantial threat that a hazardous substance will be released into the environment;
- Any pollutant or contaminant is released into the environment "which may present an imminent and substantial danger to the public health or welfare;" or
- There is a substantial threat that a pollutant or contaminant may be released into the environment "which may present an imminent and substantial danger to the public health or welfare."

Section 104(b) Investigatory Response

Under Section 104(b), the Administrator is authorized to "undertake such investigations, monitoring, surveys, testing, and other information gathering" that may be needed "to identify the existence and extent of the release or threat thereof, the source and nature of the hazardous substances, pollutants or contaminants involved, and the extent of danger to the public health or welfare or to the environment." This investigatory response can be initiated whenever the Administrator can act under Section 104(a) when he has "reason to believe" that:

- A release has occurred;
- A release is about to occur; or
- "Illness, disease, or complaints thereof may be attributed to exposure to a hazardous substance, pollutant, or contaminant and that a release may have occurred or be occurring."

Section 104(e) Information Gathering and Access

Under Section 104(e), a designated representative of the President or a state or political subdivision under a contract or cooperative agreement is authorized to obtain information and gain access to sites and adjacent property "for the purposes of determining the need for response, or choosing or taking" a response, or to enforce any provision of CERCLA. The authority to enter a site and to inspect and take samples from a site may only be exercised where "there is a reasonable basis to believe there may be a release or threat of release of a hazardous substance or pollutant or contaminant."

Access to Information. Section 104(e) authorizes any designated official, upon reasonable notice, to require persons to provide relevant information or documents concerning:

- "Identification, nature and quantity of materials which have been or are generated, treated, stored, or disposed of" at the facility;
- "The nature or extent of a release or threatened release of a hazardous substance or pollutant or contaminant at" the facility; and
- "Information relating to the ability of a person to pay or perform a cleanup."

In addition, upon reasonable notice, Section 104(e) requires persons to grant access to a facility to inspect and copy all documents or records, or at their option to provide copies.

Entry. Designated representatives are authorized to enter at reasonable times, any vessel, facility, establishment, or other place or property:

- "Where any hazardous substance, pollutant, or contaminant may be or has been generated, stored, treated, disposed of, or transported from;"
- "From which or to which a hazardous substance, pollutant, or contaminant has been or may have been released;" and
- "Where entry is needed to determine the need for response or the appropriate response or to effectuate a response action."

Compliance Orders. If consent is not granted for access to information, entry onto the facility, and inspection or sampling, Section 104(e)(5) authorizes EPA to:

- "Issue an order directing compliance with the request," after such notice and opportunity for consultation;
- Ask the Attorney General to commence a civil action to compel compliance with a request or order; and
- Assess civil penalties up to \$25,000/day for failure to comply with the order.

Section 104(e) also provides for the right to obtain access or information in any other lawful manner, which includes warrants.

Confidentiality of Information. Section 104(e)(7) provides that no person required to provide information under CERCLA may claim that such information is entitled to protection unless such person shows each of the following:

- The "person has not described the information to any other person, other than a member of a local emergency planning committee under Title III of SARA," an officer or employee of the U.S. or a state or local government, an employee of such person, or a person who is bound by a confidentiality agreement, and such person has taken reasonable measures to protect the confidentiality of such information and intends to continue to take such measures;"
- "The information is not required to be disclosed, or otherwise made available, to the public under any other federal or state law;"
- "Disclosure of the information is likely to cause substantial harm to the competitive position of such person;" and
- "The specific chemical identity, if sought to be protected, is not readily discoverable through reverse engineering."

The following information on hazardous substances is not entitled to protection:

- Trade name, common name, or generic class or category;
- Physical properties;
- Hazards to health and the environment, including physical hazards (e.g., explosion) and potential acute and chronic health hazards;
- Potential routes of human exposure;
- Disposal location of any waste stream;
- Monitoring data or analysis on disposal activities;
- Hydrogeologic or geologic data; and
- Groundwater monitoring data.

Section 106(a) Abatement Action

This section of CERCLA provides the federal government with the authority to pursue administrative and judicial action to require responsible parties to respond to actual or threatened releases of hazardous substances. If the Administrator "determines that there may be an imminent and substantial endangerment to the public health or welfare or the environment," he has two options under 106(a):

- Request the Attorney General to seek the necessary relief in the federal district court where the threat occurs. The district court is given jurisdiction to grant relief as the public interest and the equities of the case may require; or

- After providing notice to the affected state, he may take other action, including, but not limited to the issuance of orders that may be necessary to protect public health and welfare and the environment.

Note: Statutory texts of these reviewed CERCLA sections follows.

COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION AND LIABILITY

(42 U.S.C.A. §§ 9601 to 9675)

CHAPTER 103—COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION, AND LIABILITY

SUBCHAPTER I—HAZARDOUS SUBSTANCES RELEASES, LIABILITY, COMPENSATION

Sec.

9601. Definitions.
9602. Designation of additional hazardous substances and establishment of reportable released quantities; regulations.
9603. Notification requirements respecting released substances.
- (a) Notice to National Response Center upon release from vessel or offshore or onshore facility by person in charge; conveyance of notice by Center.
- (b) Penalties for failure to notify; use of notice or information pursuant to notice in criminal case.
- (c) Notice to Administrator of EPA of existence of storage, etc., facility by owner or operator; exceptions; time, manner, and form of notice; penalties for failure to notify; use of notice or information pursuant to notice in criminal case.
- (d) Recordkeeping requirements; promulgation of rules and regulations by Administrator of EPA; penalties for violations; waiver of retention requirements.
- (e) Applicability to registered pesticide product.
- (f) Exemptions from notice and penalty provisions for substances reported under other Federal law or is in continuous release, etc.
9604. Response authorities.
- (a) Removal and other remedial action by President; applicability of national contingency plan; response by potentially responsible parties; public health threats; limitations on response; exception.
- (b) Investigations, monitoring, etc., by President.
- (c) Criteria for continuance of obligations from Fund over specified amount for response actions; consultation by President with affected States; contracts or cooperative agreements by States with President prior to remedial actions; cost-sharing agreements; selection by President of remedial actions; State credits: granting of credit, expenses before listing or agreement, response actions between 1978 and 1980, State expenses after December 11, 1980, in excess of 10 percent of costs, item-by-item approval, use of credits; operation and

Sec.

9604. Response authorities—Cont'd
- maintenance; limitation on source of funds for O & M; recontracting; siting.
- (d) Contracts or cooperative agreements by President with States or political subdivisions or Indian tribes; State applications, terms and conditions; reimbursements; cost-sharing provisions; enforcement requirements and procedures.
- (e) Information gathering and access; action authorized, access to information, entry, inspection and samples; authority and samples, compliance orders; issuance and compliance, other authority, confidentiality of information; basis for withholding.
- (f) Contracts for response action; compliance with Federal health and safety standards.
- (g) Rates for wages and labor standards applicable to covered work.
- (h) Emergency procurement powers; exercise by President.
- (i) Agency for Toxic Substances and Disease Registry; establishment, functions, etc.
- (j) Acquisition of property.
9605. National contingency plan; preparation, contents, etc.
- (a) Revision and republication.
- (b) Revision of plan.
- (c) Hazard ranking system.
- (1) Revision.
- (2) Health assessment of water contamination risks.
- (3) Reevaluation not required.
- (4) New information.
- (d) Petition for assessment of release.
- (e) Releases from earlier sites.
- (f) Minority contractors.
- (g) Special study wastes.
- (1) Application.
- (2) Considerations in adding facilities to NPL.
- (3) Savings provisions.
- (4) Information gathering and analysis.
9606. Abatement actions.
- (a) Maintenance, jurisdiction, etc.
- (b) Fines; reimbursement.
- (c) Guidelines for using imminent hazard, enforcement, and emergency response authorities; promulgation by Administrator of EPA, scope, etc.
9607. Liability.
- (a) Covered persons; scope; recoverable costs and damages; interest rate; "comparable maturity" date.
- (b) Defenses.
- (c) Determination of amounts.

SUBCHAPTER IV—POLLUTION INSURANCE

Sec.

9671. Definitions.
- (1) Insurance.
 - (2) Pollution liability.
 - (3) Risk retention group.
 - (4) Purchasing group.
 - (5) State.
9672. State laws; scope of subchapter.
- (a) State laws.
 - (b) Scope of title.
9673. Risk retention groups.
- (a) Exemption.
 - (b) Exceptions.
 - (1) State laws generally applicable.
 - (2) State regulations not subject to exemption.
 - (c) Application of exemptions.
 - (d) Agents or brokers.
9674. Purchasing groups.
- (a) Exemption.
 - (b) Application of exemptions.
 - (c) Agents or brokers.
9675. Applicability of securities laws.
- (a) Ownership interests.
 - (b) Investment Company Act.
 - (c) Blue sky law.

West's Federal Forms

Administrative agency decisions and orders, enforcement and review, see § 851 et seq.
 Administrative subpoenas, enforcement, see § 6004 et seq.
 Depositions and discovery, see §§ 3271 et seq., 3681 et seq.
 Intervention, motion for leave, see § 3111 et seq.
 Jurisdiction and venue in district courts, see § 1003 et seq.
 Production of documents, motions and orders pertaining to, see § 3551 et seq.
 Sentence and fine, see § 7531 et seq.
 Subpoenas, see § 3981 et seq.

WESTLAW Electronic Research

See WESTLAW guide following the Explanation pages of this pamphlet.

SUBCHAPTER I—HAZARDOUS SUBSTANCES
RELEASES, LIABILITY, COMPENSATION

§ 9601. Definitions

For purpose of this subchapter—

(1) The term “act of God” means an unanticipated grave natural disaster or other natural phenomenon of an exceptional, inevitable, and irresistible character, the effects of which could not have been prevented or avoided by the exercise of due care or foresight.

(2) The term “Administrator” means the Administrator of the United States Environmental Protection Agency.

(3) The term “barrel” means forty-two United States gallons at sixty degrees Fahrenheit.

(4) The term “claim” means a demand in writing for a sum certain.

(5) The term “claimant” means any person who presents a claim for compensation under this chapter.

(6) The term “damages” means damages for injury or loss of natural resources as set forth in section 9607(a) or 9611(b) of this title.

(7) The term “drinking water supply” means any raw or finished water source that is or may be used by a public water system (as defined in the Safe Drinking Water Act [42 U.S.C. 300f et seq.]) or as drinking water by one or more individuals.

(8) The term “environment” means (A) the navigable waters, the waters of the contiguous zone, and the ocean waters for which the natural resources are under the exclusive management authority of the United States under the Magnuson Fishery Conservation and Management Act [16 U.S.C. 1801 et seq.], and (B) any other surface water, ground water, drinking water supply, land surface or subsurface strata, or ambient air within the United States or under the jurisdiction of the United States.

(9) The term “facility” means (A) any building, structure, installation, equipment, pipe or pipeline (including any pipe into a sewer or publicly owned treatment works), well, pit, pond, lagoon, impoundment, ditch, landfill, storage container, motor vehicle, rolling stock, or aircraft, or (B) any site or area where a hazardous substance has been deposited, stored, disposed of, or placed, or otherwise come to be located; but does not include any consumer product in consumer use or any vessel.

(10) The term “federally permitted release” means (A) discharges in compliance with a permit under section 1342 of Title 33, (B) discharges resulting from circumstances identified and reviewed and made part of the public record with respect to a permit issued or modified under section 1342 of Title 33 and subject to a condition of such permit, (C) continuous or anticipated intermittent discharges from a point source, identified in a permit or permit application under section 1342 of Title 33, which are caused by events occurring within the scope of relevant operating or treatment systems, (D) discharges in compliance with a legally enforceable permit under section 1344 of Title 33, (E) releases in compliance with a legally enforceable final permit issued pursuant to section 3005(a) through (d) of the Solid Waste Disposal Act [42 U.S.C. 6925(a) to (d)] from a hazardous waste treatment, storage, or disposal facility when such permit specifically

identifies the hazardous substances and makes such substances subject to a standard of practice, control procedure or bioassay limitation or condition, or other control on the hazardous substances in such releases, (F) any release in compliance with a legally enforceable permit issued under section 1412 of Title 33 or¹ section 1413 of Title 33, (G) any injection of fluids authorized under Federal underground injection control programs or State programs submitted for Federal approval (and not disapproved by the Administrator of the Environmental Protection Agency) pursuant to part C of the Safe Drinking Water Act [42 U.S.C. 300h et seq.], (H) any emission into the air subject to a permit or control regulation under section 111 [42 U.S.C. 7411], section 112 [42 U.S.C. 7412], Title I part C [42 U.S.C. 7470 et seq.], Title I part D [42 U.S.C. 7501 et seq.], or State implementation plans submitted in accordance with section 110 of the Clean Air Act [42 U.S.C. 7410] (and not disapproved by the administrator of the Environmental Protection Agency), including any schedule or waiver granted, promulgated, or approved under these sections, (I) any injection of fluids or other materials authorized under applicable State law (i) for the purpose of stimulating or treating wells for the production of crude oil, natural gas, or water, (ii) for the purpose of secondary, tertiary, or other enhanced recovery of crude oil or natural gas, or (iii) which are brought to the surface in conjunction with the production of crude oil or natural gas and which are reinjected, (J) the introduction of any pollutant into a publicly owned treatment works when such pollutant is specified in and in compliance with applicable pretreatment standards of section 1317(b) or (c) of Title 33 and enforceable requirements in a pretreatment program submitted by a State or municipality for Federal approval under section 1342 of Title 33, and (K) any release of source, special nuclear, or byproduct material, as those terms are defined in the Atomic Energy Act of 1954 [42 U.S.C. 2011 et seq.], in compliance with a legally enforceable license, permit, regulation, or order issued pursuant to the Atomic Energy Act of 1954.

(11) The term "Fund" or "Trust Fund" means the Hazardous Substance Superfund established by section 9507 of Title 26.

(12) The term "ground water" means water in a saturated zone or stratum beneath the surface of land or water.

(13) The term "guarantor" means any person, other than the owner or operator, who provides evidence of financial responsibility for an owner or operator under this chapter.

(14) The term "hazardous substance" means (A) any substance designated pursuant to section 1321(b)(2)(A) of Title 33, (B) any element, compound, mixture, solution, or substance designated pursuant to section 9602 of this title, (C) any hazardous waste having the characteristics identified under or listed pursuant to section 3001 of the Solid Waste Disposal Act [42 U.S.C. 6921] (but not including any waste the regulation of which under the Solid Waste Disposal Act [42 U.S.C. 6901 et seq.] has been suspended by Act of Congress), (D) any toxic pollutant listed under section 1317(a) of Title 33, (E) any hazardous air pollutant listed under section 112 of the Clean Air Act [42 U.S.C. 7412], and (F) any imminently hazardous chemical substance or mixture with respect to which the Administrator has taken action pursuant to section 2606 of Title 15. The term does not include petroleum, including crude oil or any fraction thereof which is not otherwise specifically listed or designated as a hazardous substance under subparagraphs (A) through (F) of this paragraph, and the term does not include natural gas, natural gas liquids, liquefied natural gas, or synthetic gas usable for fuel (or mixtures of natural gas and such synthetic gas).

(15) The term "navigable waters" or "navigable waters of the United States" means the waters of the United States, including the territorial seas.

(16) The term "natural resources" means land, fish, wildlife, biota, air, water, ground water, drinking water supplies, and other such resources belonging to, managed by, held in trust by, appertaining to, or otherwise controlled by the United States (including the resources of the fishery conservation zone established by the Magnuson Fishery Conservation and Management Act [16 U.S.C. 1801 et seq.]) any State or local government, any foreign government, any Indian tribe, or, if such resources are subject to a trust restriction on alienation, any member of an Indian tribe.

(17) The term "offshore facility" means any facility of any kind located in, on, or under, any of the navigable waters of the United States, and any facility of any kind which is subject to the jurisdiction of the United States and is located in, on, or under any other waters, other than a vessel or a public vessel.

(18) The term "onshore facility" means any facility (including, but not limited to, motor vehicles and rolling stock) of any kind located in, on, or under, any land or nonnavigable waters within the United States.

(19) The term "otherwise subject to the jurisdiction of the United States" means subject to the

jurisdiction of the United States by virtue of United States citizenship, United States vessel documentation or numbering, or as provided by international agreement to which the United States is a party.

(20)(A) The term "owner or operator" means (i) in the case of a vessel, any person owning, operating, or chartering by demise, such vessel, (ii) in the case of an onshore facility or an offshore facility, any person owning or operating such facility, and (iii) in the case of any facility, title or control of which was conveyed due to bankruptcy, foreclosure, tax delinquency, abandonment, or similar means to a unit of State or local government, any person who owned, operated or otherwise controlled activities at such facility immediately beforehand. Such term does not include a person, who, without participating in the management of a vessel or facility, holds indicia of ownership primarily to protect his security interest in the vessel or facility.

(B) In the case of a hazardous substance which has been accepted for transportation by a common or contract carrier and except as provided in section 9607(a)(3) or (4) of this title, (i) the term "owner or operator" shall mean such common carrier or other bona fide for hire carrier acting as an independent contractor during such transportation, (ii) the shipper of such hazardous substance shall not be considered to have caused or contributed to any release during such transportation which resulted solely from circumstances or conditions beyond his control.

(C) In the case of a hazardous substance which has been delivered by a common or contract carrier to a disposal or treatment facility and except as provided in section 9607(a)(3) or (4) of this title (i) the term "owner or operator" shall not include such common or contract carrier, and (ii) such common or contract carrier shall not be considered to have caused or contributed to any release at such disposal or treatment facility resulting from circumstances or conditions beyond its control.

(D) The term "owner or operator" does not include a unit of State or local government which acquired ownership or control involuntarily through bankruptcy, tax delinquency, abandonment, or other circumstances in which the government involuntarily acquires title by virtue of its function as sovereign. The exclusion provided under this paragraph shall not apply to any State or local government which has caused or contributed to the release or threatened release of a hazardous substance from the facility, and such a State or local government shall be subject to the provisions of this chapter in the same manner and to the same extent, both procedurally and sub-

stantively, as any nongovernmental entity, including liability under section 9607 of this title.

(21) The term "person" means an individual, firm, corporation, association, partnership, consortium, joint venture, commercial entity, United States Government, State, municipality, commission, political subdivision of a State, or any interstate body.

(22) The term "release" means any spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of barrels, containers, and other closed receptacles containing any hazardous substance or pollutant or contaminant), but excludes (A) any release which results in exposure to persons solely within a workplace, with respect to a claim which such persons may assert against the employer of such persons, (B) emissions from the engine exhaust of a motor vehicle, rolling stock, aircraft, vessel, or pipeline pumping station engine, (C) release of source, byproduct, or special nuclear material from a nuclear incident, as those terms are defined in the Atomic Energy Act of 1954 [42 U.S.C. 2011 et seq.], if such release is subject to requirements with respect to financial protection established by the Nuclear Regulatory Commission under section 170 of such Act [42 U.S.C. 2210], or, for the purposes of section 9604 of this title or any other response action, any release of source byproduct, or special nuclear material from any processing site designated under section 7912(a)(1) or 7942(a) of this title, and (D) the normal application of fertilizer.

(23) The term "remove" or "removal" means the cleanup or removal of released hazardous substances from the environment, such actions as may be necessary² taken in the event of the threat of release of hazardous substances into the environment, such actions as may be necessary to monitor, assess, and evaluate the release or threat or release of hazardous substances, the disposal of removed material, or the taking of such other actions as may be necessary to prevent, minimize, or mitigate damage to the public health or welfare or to the environment, which may otherwise result from a release or threat of release. The term includes, in addition, without being limited to, security fencing or other measures to limit access, provision of alternative water supplies, temporary evacuation and housing of threatened individuals not otherwise provided for, action taken under section 9604(b) of this title, and any emergency assistance which may be provided under the Disaster Relief Act of 1974 [42 U.S.C. 5121 et seq.].

(24) The term "remedy" or "remedial action" means those actions consistent with permanent

remedy taken instead of or in addition to removal actions in the event of a release or threatened release of a hazardous substance into the environment, to prevent or minimize the release of hazardous substances so that they do not migrate to cause substantial danger to present or future public health or welfare or the environment. The term includes, but is not limited to, such actions at the location of the release as storage, confinement, perimeter protection using dikes, trenches, or ditches, clay cover, neutralization, cleanup of released hazardous substances or contaminated materials, recycling or reuse, diversion, destruction, segregation of reactive wastes, dredging or excavations, repair or replacement of leaking containers, collection of leachate and runoff, onsite treatment or incineration, provision of alternative water supplies, and any monitoring reasonably required to assure that such actions protect the public health and welfare and the environment. The term includes the costs of permanent relocation of residents and businesses and community facilities where the President determines that, alone or in combination with other measures, such relocation is more cost-effective than and environmentally preferable to the transportation, storage, treatment, destruction, or secure disposition offsite of hazardous substances, or may otherwise be necessary to protect the public health or welfare; the term includes offsite transport and offsite storage, treatment, destruction, or secure disposition of hazardous substances and associated contaminated materials.

(25) The term "respond" or "response" means remove, removal, remedy, and remedial action, all such terms (including the terms "removal" and "remedial action") include enforcement activities related thereto.

(26) The term "transport" or "transportation" means the movement of a hazardous substance by any mode, including pipeline (as defined in the Pipeline Safety Act), and in the case of a hazardous substance which has been accepted for transportation by a common or contract carrier, the term "transport" or "transportation" shall include any stoppage in transit which is temporary, incidental to the transportation movement, and at the ordinary operating convenience of a common or contract carrier, and any such stoppage shall be considered as a continuity of movement and not as the storage of a hazardous substance.

(27) The terms "United States" and "State" include the several States of the United States, the District of Columbia, the Commonwealth of Puerto Rico, Guam, American Samoa, the United States Virgin Islands, the Commonwealth of the Northern Marianas, and any other territory or

possession over which the United States has jurisdiction.

(28) The term "vessel" means every description of watercraft or other artificial contrivance used, or capable of being used, as a means of transportation on water.

(29) The terms "disposal", "hazardous waste", and "treatment" shall have the meaning provided in section 1004 of the Solid Waste Disposal Act [42 U.S.C. 6903].

(30) The terms "territorial sea" and "contiguous zone" shall have the meaning provided in section 1362 of Title 33.

(31) The term "national contingency plan" means the national contingency plan published under section 1321(c) of Title 33 or revised pursuant to section 9605 of this title.

(32) The term "liable" or "liability" under this subchapter shall be construed to be the standard of liability which obtains under section 1321 of Title 33.

(33) The term "pollutant or contaminant" shall include, but not be limited to, any element, substance, compound, or mixture, including disease-causing agents, which after release into the environment and upon exposure, ingestion, inhalation, or assimilation into any organism, either directly from the environment or indirectly by ingestion through food chains, will or may reasonably be anticipated to cause death, disease, behavioral abnormalities, cancer, genetic mutation, physiological malfunctions (including malfunctions in reproduction) or physical deformations, in such organisms or their offspring; except that the term "pollutant or contaminant" shall not include petroleum, including crude oil or any fraction thereof which is not otherwise specifically listed or designated as a hazardous substance under subparagraphs (A) through (F) of paragraph (14) and shall not include natural gas, liquefied natural gas, or synthetic gas of pipeline quality (or mixtures of natural gas and such synthetic gas).

(34) The term "alternative water supplies" includes, but is not limited to, drinking water and household water supplies.

(35)(A) The term "contractual relationship", for the purpose of section 9607(b)(3) of this title includes, but is not limited to, land contracts, deeds or other instruments transferring title or possession, unless the real property on which the facility concerned is located was acquired by the defendant after the disposal or placement of the hazardous substance on, in, or at the facility, and one or more of the circumstances described in clause (i), (ii), or (iii) is also established by the defendant by a preponderance of the evidence:

(i) At the time the defendant acquired the facility the defendant did not know and had no reason to know that any hazardous substance which is the subject of the release or threatened release was disposed of on, in, or at the facility.

(ii) The defendant is a government entity which acquired the facility by escheat, or through any other involuntary transfer or acquisition, or through the exercise of eminent domain authority by purchase or condemnation.

(iii) The defendant acquired the facility by inheritance or bequest.

In addition to establishing the foregoing, the defendant must establish that he has satisfied the requirements of section 9607(b)(3)(a) and (b) of this title.

(B) To establish that the defendant had no reason to know, as provided in clause (i) of subparagraph (A) of this paragraph, the defendant must have undertaken, at the time of acquisition, all appropriate inquiry into the previous ownership and uses of the property consistent with good commercial or customary practice in an effort to minimize liability. For purposes of the preceding sentence the court shall take into account any specialized knowledge or experience on the part of the defendant, the relationship of the purchase price to the value of the property if uncontaminated, commonly known or reasonably ascertainable information about the property, the obviousness of the presence or likely presence of contamination at the property, and the ability to detect such contamination by appropriate inspection.

(C) Nothing in this paragraph or in section 9607(b)(3) of this title shall diminish the liability of any previous owner or operator of such facility who would otherwise be liable under this chapter. Notwithstanding this paragraph, if the defendant obtained actual knowledge of the release or threatened release of a hazardous substance at such facility when the defendant owned the real property and then subsequently transferred ownership of the property to another person without disclosing such knowledge, such defendant shall be treated as liable under section 9607(a)(1) of this title and no defense under section 9607(b)(3) of this title shall be available to such defendant.

(D) Nothing in this paragraph shall affect the liability under this chapter of a defendant who, by any act or omission, caused or contributed to the release or threatened release of a hazardous substance which is the subject of the action relating to the facility.

(36) The term "Indian tribe" means any Indian tribe, band, nation, or other organized group or community, including any Alaska Native village but not including any Alaska Native regional or village corporation, which is recognized as eligible for the special programs and services provided by the United States to Indians because of their status as Indians.

(37)(A) The term "service station dealer" means any person—

(i) who owns or operates a motor vehicle service station, filling station, garage, or similar retail establishment engaged in the business of selling, repairing, or servicing motor vehicles, where a significant percentage of the gross revenue of the establishment is derived from the fueling, repairing, or servicing of motor vehicles, and

(ii) who accepts for collection, accumulation, and delivery to an oil recycling facility, recycled oil that (I) has been removed from the engine of a light duty motor vehicle or household appliances by the owner of such vehicle or appliances, and (II) is presented, by such owner, to such person for collection, accumulation, and delivery to an oil recycling facility.

(B) For purposes of section 9614(c) of this title the term "service station dealer" shall, notwithstanding the provisions of subparagraph (A), include any government agency that establishes a facility solely for the purpose of accepting recycled oil that satisfies the criteria set forth in subclauses (I) and (II) of subparagraph (A)(ii), and, with respect to recycled oil that satisfies the criteria set forth in subclauses (I) and (II), owners or operators of refuse collection services who are compelled by State law to collect, accumulate, and deliver such oil to an oil recycling facility.

(C) The President shall promulgate regulations regarding the determination of what constitutes a significant percentage of the gross revenues of an establishment for purposes of this paragraph.

(38) The term "incineration vessel" means any vessel which carries hazardous substances for the purpose of incineration of such substances, so long as such substances or residues of such substances are on board.

(Dec. 11, 1980, Pub.L. 96-510, Title I, § 101, 94 Stat. 2767; Dec. 22, 1980, Pub.L. 96-561, Title II, § 238(b), 94 Stat. 3300; as amended Oct. 17, 1986, Pub.L. 99-499, Title I, §§ 101, 114(b), 127(a), Title V, § 517(c)(2), 100 Stat. 1615, 1652, 1692, 1774.)

¹ So in original. Probably should be "or".

² So in original. Probably should be "necessarily".

(e) Applicability to registered pesticide product

This section shall not apply to the application of a pesticide product registered under the Federal Insecticide, Fungicide, and Rodenticide Act [7 U.S.C. 136 et seq.] or to the handling and storage of such a pesticide product by an agricultural producer.

(f) Exemptions from notice and penalty provisions for substances reported under other Federal law or is in continuous release, etc.

No notification shall be required under subsection (a) or (b) of this section for any release of a hazardous substance—

(1) which is required to be reported (or specifically exempted from a requirement for reporting) under subtitle C of the Solid Waste Disposal Act [42 U.S.C. 6921 et seq.] or regulations thereunder and which has been reported to the National Response Center, or

(2) which is a continuous release, stable in quantity and rate, and is—

(A) from a facility for which notification has been given under subsection (c) of this section, or

(B) a release of which notification has been given under subsections (a) and (b) of this section for a period sufficient to establish the continuity, quantity, and regularity of such release:

Provided, That notification in accordance with subsections (a) and (b) of this paragraph shall be given for releases subject to this paragraph annually, or at such time as there is any statistically significant increase in the quantity of any hazardous substance or constituent thereof released, above that previously reported or occurring.

(Dec. 11, 1980, Pub.L. 96-510, Title I, § 103, 94 Stat. 2772; Dec. 22, 1980, Pub.L. 96-561, Title II, § 238(b), 94 Stat. 3300; as amended Oct. 17, 1986, Pub.L. 99-499, Title I, §§ 103, 109(a)(1), (2), 100 Stat. 1617, 1632, 1633.)

Library References

Health and Environment ⇐ 25.5(10), 25.6(3), (9), 25.7(3), (24).
C.J.S. Health and Environment §§ 92, 103 et seq., 106, 113 et seq.

§ 9604. Response authorities**(a) Removal and other remedial action by President; applicability of national contingency plan; response by potentially responsible parties; public health threats; limitations on response: exception**

(1) Whenever (A) any hazardous substance is released or there is a substantial threat of such a release into the environment, or (B) there is a release or substantial threat of release into the environment of any pollutant or contaminant which may present an imminent and substantial danger to the

public health or welfare, the President is authorized to act, consistent with the national contingency plan, to remove or arrange for the removal of, and provide for remedial action relating to such hazardous substance, pollutant, or contaminant at any time (including its removal from any contaminated natural resource), or take any other response measure consistent with the national contingency plan which the President deems necessary to protect the public health or welfare or the environment. When the President determines that such action will be done properly and promptly by the owner or operator of the facility or vessel or by any other responsible party, the President may allow such person to carry out the action, conduct the remedial investigation, or conduct the feasibility study in accordance with section 9622 of this title. No remedial investigation or feasibility study (RI/FS) shall be authorized except on a determination by the President that the party is qualified to conduct the RI/FS and only if the President contracts with or arranges for a qualified person to assist the President in overseeing and reviewing the conduct of such RI/FS and if the responsible party agrees to reimburse the Fund for any cost incurred by the President under, or in connection with, the oversight contract or arrangement. In no event shall a potentially responsible party be subject to a lesser standard of liability, receive preferential treatment, or in any other way, whether direct or indirect, benefit from any such arrangements as a response action contractor, or as a person hired or retained by such a response action contractor, with respect to the release or facility in question. The President shall give primary attention to those releases which the President deems may present a public health threat.

(2) Removal action

Any removal action undertaken by the President under this subsection (or by any other person referred to in section 9622 of this title) should, to the extent the President deems practicable, contribute to the efficient performance of any long term remedial action with respect to the release or threatened release concerned.

(3) Limitations on response

The President shall not provide for a removal or remedial action under this section in response to a release or threat of release—

(A) of a naturally occurring substance in its unaltered form, or altered solely through naturally occurring processes or phenomena, from a location where it is naturally found;

(B) from products which are part of the structure of, and result in exposure within, residential buildings or business or community structures; or

(C) into public or private drinking water supplies due to deterioration of the system through ordinary use.

(4) Exception to limitations

Notwithstanding paragraph (3) of this subsection, to the extent authorized by this section, the President may respond to any release or threat of release if in the President's discretion, it constitutes a public health or environmental emergency and no other person with the authority and capability to respond to the emergency will do so in a timely manner.

(b) Investigations, monitoring, etc., by President

(1) Information; studies and investigations

Whenever the President is authorized to act pursuant to subsection (a) of this section, or whenever the President has reason to believe that a release has occurred or is about to occur, or that illness, disease, or complaints thereof may be attributable to exposure to a hazardous substance, pollutant, or contaminant and that a release may have occurred or be occurring, he may undertake such investigations, monitoring, surveys, testing, and other information gathering as he may deem necessary or appropriate to identify the existence and extent of the release or threat thereof, the source and nature of the hazardous substances, pollutants or contaminants involved, and the extent of danger to the public health or welfare or to the environment. In addition, the President may undertake such planning, legal, fiscal, economic, engineering, architectural, and other studies or investigations as he may deem necessary or appropriate to plan and direct response actions, to recover the costs thereof, and to enforce the provisions of this chapter.

(2) Coordination of investigations

The President shall promptly notify the appropriate Federal and State natural resource trustees of potential damages to natural resources resulting from releases under investigation pursuant to this section and shall seek to coordinate the assessments, investigations, and planning under this section with such Federal and State trustees.

(c) Criteria for continuance of obligations from Fund over specified amount for response actions; consultation by President with affected States; contracts or cooperative agreements by States with President prior to remedial actions; cost-sharing agreements; selection by President of remedial actions; State credits: granting of credit, expenses before listing or agreement, response actions between 1978 and 1980. State expenses after December 11, 1980, in excess of 10 percent of costs, item-by-item approval, use of credits; operation and maintenance; limitation on source of funds for O&M; recontracting; siting

(1) Unless (A) the President finds that (i) continued response actions are immediately required to

prevent, limit, or mitigate an emergency, (ii) there is an immediate risk to public health or welfare or the environment, and (iii) such assistance will not otherwise be provided on a timely basis, or (B) the President has determined the appropriate remedial actions pursuant to paragraph (2) of this subsection and the State or States in which the source of the release is located have complied with the requirements of paragraph (3) of this subsection, or (C) continued response action is otherwise appropriate and consistent with the remedial action to be taken¹ obligations from the Fund, other than those authorized by subsection (b) of this section, shall not continue after \$2,000,000 has been obligated for response actions or 12 months has elapsed from the date of initial response to a release or threatened release of hazardous substances.

(2) The President shall consult with the affected State or States before determining any appropriate remedial action to be taken pursuant to the authority granted under subsection (a) of this section.

(3) The President shall not provide any remedial actions pursuant to this section unless the State in which the release occurs first enters into a contract or cooperative agreement with the President providing assurances deemed adequate by the President that (A) the State will assure all future maintenance of the removal and remedial actions provided for the expected life of such actions as determined by the President; (B) the State will assure the availability of a hazardous waste disposal facility acceptable to the President and in compliance with the requirements of subtitle C of the Solid Waste Disposal Act [42 U.S.C.A. § 6921 et seq.] for any necessary off-site storage, destruction, treatment, or secure disposition of the hazardous substances; and (C) the State will pay or assure payment of (i) 10 per centum of the costs of the remedial action, including all future maintenance, or (ii) 50 percent (or such greater amount as the President may determine appropriate, taking into account the degree of responsibility of the State or political subdivision for the release) of any sums expended in response to a release at a facility, that was operated by the State or a political subdivision thereof, either directly or through a contractual relationship or otherwise, at the time of any disposal of hazardous substances therein. For the purpose of clause (ii) of this subparagraph, the term "facility" does not include navigable waters or the beds underlying those waters. The President shall grant the State a credit against the share of the costs for which it is responsible under this paragraph for any documented direct out-of-pocket non-Federal funds expended or obligated by the State or a political subdivision thereof after January 1, 1978, and before December 11, 1980, for cost-eligible response actions and claims

vene in any civil action involving the enforcement of such contract or subcontract.

(4) Where two or more noncontiguous facilities are reasonably related on the basis of geography, or on the basis of the threat, or potential threat to the public health or welfare or the environment, the President may, in his discretion, treat these related facilities as one for purposes of this section.

(e) Information gathering and access; action authorized, access to information, entry, inspection and samples; authority and samples, compliance orders; issuance and compliance, other authority, confidentiality of information; basis for withholding

(1) Action authorized

Any officer, employee, or representative of the President, duly designated by the President, is authorized to take action under paragraph (2), (3), or (4) (or any combination thereof) at a vessel, facility, establishment, place, property, or location or, in the case of paragraph (3) or (4), at any vessel, facility, establishment, place, property, or location which is adjacent to the vessel, facility, establishment, place, property, or location referred to in such paragraph (3) or (4). Any duly designated officer, employee, or representative of a State or political subdivision under a contract or cooperative agreement under subsection (d)(1) of this section is also authorized to take such action. The authority of paragraphs (3) and (4) may be exercised only if there is a reasonable basis to believe there may be a release or threat of release of a hazardous substance or pollutant or contaminant. The authority of this subsection may be exercised only for the purposes of determining the need for response, or choosing or taking any response action under this subchapter, or otherwise enforcing the provisions of this subchapter.

(2) Access to information

Any officer, employee, or representative described in paragraph (1) may require any person who has or may have information relevant to any of the following to furnish, upon reasonable notice, information or documents relating to such matter:

(A) The identification, nature, and quantity of materials which have been or are generated, treated, stored, or disposed of at a vessel or facility or transported to a vessel or facility.

(B) The nature or extent of a release or threatened release of a hazardous substance or pollutant or contaminant at or from a vessel or facility.

(C) Information relating to the ability of a person to pay for or to perform a cleanup.

In addition, upon reasonable notice, such person either (i) shall grant any such officer, employee, or representative access at all reasonable times to any vessel, facility, establishment, place, property, or location to inspect and copy all documents or records relating to such matters or (ii) shall copy and furnish to the officer, employee, or representative all such documents or records, at the option and expense of such person.

(3) Entry

Any officer, employee, or representative described in paragraph (1) is authorized to enter at reasonable times any of the following:

(A) Any vessel, facility, establishment, or other place or property where any hazardous substance or pollutant or contaminant may be or has been generated, stored, treated, disposed of, or transported from.

(B) Any vessel, facility, establishment, or other place or property from which or to which a hazardous substance or pollutant or contaminant has been or may have been released.

(C) Any vessel, facility, establishment, or other place or property where such release is or may be threatened.

(D) Any vessel, facility, establishment, or other place or property where entry is needed to determine the need for response or the appropriate response or to effectuate a response action under this subchapter.

(4) Inspection and samples

(A) Authority

Any officer, employee or representative described in paragraph (1) is authorized to inspect and obtain samples from any vessel, facility, establishment, or other place or property referred to in paragraph (3) or from any location of any suspected hazardous substance or pollutant or contaminant. Any such officer, employee, or representative is authorized to inspect and obtain samples of any containers or labeling for suspected hazardous substances or pollutants or contaminants. Each such inspection shall be completed with reasonable promptness.

(B) Samples

If the officer, employee, or representative obtains any samples, before leaving the premises he shall give to the owner, operator, tenant, or other person in charge of the place from which the samples were obtained a receipt describing the sample obtained and, if requested, a portion of each such sample. A copy of the results of any analysis made of such samples shall be furnished promptly to the owner, oper-

ator, tenant, or other person in charge, if such person can be located.

(5) Compliance orders

(A) Issuance

If consent is not granted regarding any request made by an officer, employee, or representative under paragraph (2), (3), or (4), the President may issue an order directing compliance with the request. The order may be issued after such notice and opportunity for consultation as is reasonably appropriate under the circumstances.

(B) Compliance

The President may ask the Attorney General to commence a civil action to compel compliance with a request or order referred to in subparagraph (A). Where there is a reasonable basis to believe there may be a release or threat of a release of a hazardous substance or pollutant or contaminant, the court shall take the following actions:

(i) In the case of interference with entry or inspection, the court shall enjoin such interference or direct compliance with orders to prohibit interference with entry or inspection unless under the circumstances of the case the demand for entry or inspection is arbitrary and capricious, an abuse of discretion, or otherwise not in accordance with law.

(ii) In the case of information or document requests or orders, the court shall enjoin interference with such information or document requests or orders or direct compliance with the requests or orders to provide such information or documents unless under the circumstances of the case the demand for information or documents is arbitrary and capricious, an abuse of discretion, or otherwise not in accordance with law.

The court may assess a civil penalty not to exceed \$25,000 for each day of noncompliance against any person who unreasonably fails to comply with the provisions of paragraph (2), (3), or (4) or an order issued pursuant to subparagraph (A) of this paragraph.

(6) Other authority

Nothing in this subsection shall preclude the President from securing access or obtaining information in any other lawful manner.

(7) Confidentiality of information

(A) Any records, reports, or information obtained from any person under this section (includ-

ing records, reports, or information obtained by representatives of the President) shall be available to the public, except that upon a showing satisfactory to the President (or the State, as the case may be) by any person that records, reports, or information, or particular part thereof (other than health or safety effects data), to which the President (or the State, as the case may be) or any officer, employee, or representative has access under this section if made public would divulge information entitled to protection under section 1905 of Title 18, such information or particular portion thereof shall be considered confidential in accordance with the purposes of that section, except that such record, report, document or information may be disclosed to other officers, employees, or authorized representatives of the United States concerned with carrying out this chapter, or when relevant in any proceeding under this chapter.

(B) Any person not subject to the provisions of section 1905 of Title 18 who knowingly and willfully divulges or discloses any information entitled to protection under this subsection shall, upon conviction, be subject to a fine of not more than \$5,000 or to imprisonment not to exceed one year, or both.

(C) In submitting data under this chapter, a person required to provide such data may (i) designate the data which such person believes is entitled to protection under this subsection and (ii) submit such designated data separately from other data submitted under this chapter. A designation under this paragraph shall be made in writing and in such manner as the President may prescribe by regulation.

(D) Notwithstanding any limitation contained in this section or any other provision of law, all information reported to or otherwise obtained by the President (or any representative of the President) under this chapter shall be made available, upon written request of any duly authorized committee of the Congress, to such committee.

(E) No person required to provide information under this chapter may claim that the information is entitled to protection under this paragraph unless such person shows each of the following:

(i) Such person has not disclosed the information to any other person, other than a member of a local emergency planning committee established under title III of the Amendments and Reauthorization Act of 1986 [42 U.S.C.A. § 11001 et seq.], an officer or employee of the United States or a State or local government, an employee of such person, or a person who is bound by a confidentiality agreement, and such

person has taken reasonable measures to protect the confidentiality of such information and intends to continue to take such measures.

(ii) The information is not required to be disclosed, or otherwise made available, to the public under any other Federal or State law.

(iii) Disclosure of the information is likely to cause substantial harm to the competitive position of such person.

(iv) The specific chemical identity, if sought to be protected, is not readily discoverable through reverse engineering.

(F) The following information with respect to any hazardous substance at the facility or vessel shall not be entitled to protection under this paragraph:

(i) The trade name, common name, or generic class or category of the hazardous substance.

(ii) The physical properties of the substance, including its boiling point, melting point, flash point, specific gravity, vapor density, solubility in water, and vapor pressure at 20 degrees Celsius.

(iii) The hazards to health and the environment posed by the substance, including physical hazards (such as explosion) and potential acute and chronic health hazards.

(iv) The potential routes of human exposure to the substance at the facility, establishment, place, or property being investigated, entered, or inspected under this subsection.

(v) The location of disposal of any waste stream.

(vi) Any monitoring data or analysis of monitoring data pertaining to disposal activities.

(vii) Any hydrogeologic or geologic data.

(viii) Any groundwater monitoring data.

(f) Contracts for response action; compliance with Federal health and safety standards

In awarding contracts to any person engaged in response actions, the President or the State, in any case where it is awarding contracts pursuant to a contract entered into under subsection (d) of this section, shall require compliance with Federal health and safety standards established under section 9651(f) of this title by contractors and subcontractors as a condition of such contracts.

(g) Rates for wages and labor standards applicable to covered work

(1) All laborers and mechanics employed by contractors or subcontractors in the performance of construction, repair, or alteration work funded in whole or in part under this section shall be paid

wages at rates not less than those prevailing on projects of a character similar in the locality as determined by the Secretary of Labor in accordance with the Davis-Bacon Act [40 U.S.C. 276a et seq.]. The President shall not approve any such funding without first obtaining adequate assurance that required labor standards will be maintained upon the construction work.

(2) The Secretary of Labor shall have, with respect to the labor standards specified in paragraph (1), the authority and functions set forth in Reorganization Plan Numbered 14 of 1950 (15 F.R. 3176; 64 Stat. 1267) and section 276c of Title 40.

(h) Emergency procurement powers; exercise by President

Notwithstanding any other provision of law, subject to the provisions of section 9611 of this title, the President may authorize the use of such emergency procurement powers as he deems necessary to effect the purpose of this chapter. Upon determination that such procedures are necessary, the President shall promulgate regulations prescribing the circumstances under which such authority shall be used and the procedures governing the use of such authority.

(i) Agency for Toxic Substances and Disease Registry; establishment, functions, etc.

(1) There is hereby established within the Public Health Service an agency, to be known as the Agency for Toxic Substances and Disease Registry, which shall report directly to the Surgeon General of the United States. The Administrator of said Agency shall, with the cooperation of the Administrator of the Environmental Protection Agency, the Commissioner of the Food and Drug Administration, the Directors of the National Institute of Medicine, National Institute of Environmental Health Sciences, National Institute of Occupational Safety and Health, Centers for Disease Control, the Administrator of the Occupational Safety and Health Administration, the Administrator of the Social Security Administration, the Secretary of Transportation, and appropriate State and local health officials, effectuate and implement the health related authorities of this chapter. In addition, said Administrator shall—

(A) in cooperation with the States, establish and maintain a national registry of serious diseases and illnesses and a national registry of persons exposed to toxic substances;

(B) establish and maintain inventory of literature, research, and studies on the health effects of toxic substances;

(C) in cooperation with the States, and other agencies of the Federal Government, establish

health or the environment posed by the release of such hazardous constituents at such facility. This subparagraph refers only to available information on actual concentrations of hazardous substances and not on the total quantity of special study waste at such facility.

(3) **Savings provisions**

Nothing in this subsection shall be construed to limit the authority of the President to remove any facility which as of October 17, 1986 is included on the National Priorities List from such list, or not to list any facility which as of such date is proposed for inclusion on such list.

(4) **Information gathering and analysis**

Nothing in this chapter shall be construed to preclude the expenditure of monies from the Fund for gathering and analysis of information which will enable the President to consider the specific factors required by paragraph (2).

(Dec. 11, 1980, Pub.L. 96-510, Title I, § 105, 94 Stat. 2779, as amended Oct. 17, 1986, Pub.L. 99-499, Title I, § 105, 100 Stat. 1625.)

Code of Federal Regulations

Oil and hazardous substances pollution contingency plan, see 40 CFR 300.1 et seq.

Library References

Health and Environment — 25.6, 25.7.

C.J.S. Health and Environment §§ 91 et seq., 106 et seq.

§ 9606. Abatement actions

(a) **Maintenance, jurisdiction, etc.**

In addition to any other action taken by a State or local government, when the President determines that there may be an imminent and substantial endangerment to the public health or welfare or the environment because of an actual or threatened release of a hazardous substance from a facility, he may require the Attorney General of the United States to secure such relief as may be necessary to abate such danger or threat, and the district court of the United States in the district in which the threat occurs shall have jurisdiction to grant such relief as the public interest and the equities of the case may require. The President may also, after notice to the affected State, take other action under this section including, but not limited to, issuing such orders as may be necessary to protect public health and welfare and the environment.

(b) **Fines: reimbursement**

(1) Any person who, without sufficient cause, willfully violates, or fails or refuses to comply with, any order of the President under subsection (a) of this section may, in an action brought in the appropriate United States district court to enforce such

order, be fined not more than \$25,000 for each day in which such violation occurs or such failure to comply continues.

(2)(A) Any person who receives and complies with the terms of any order issued under subsection (a) of this section may, within 60 days after completion of the required action, petition the President for reimbursement from the Fund for the reasonable costs of such action, plus interest. Any interest payable under this paragraph shall accrue on the amounts expended from the date of expenditure at the same rate as specified for interest on investments of the Hazardous Substance Superfund established under subchapter A of chapter 98 of Title 26.

(B) If the President refuses to grant all or part of a petition made under this paragraph, the petitioner may within 30 days of receipt of such refusal file an action against the President in the appropriate United States district court seeking reimbursement from the Fund.

(C) Except as provided in subparagraph (D), to obtain reimbursement, the petitioner shall establish by a preponderance of the evidence that it is not liable for response costs under section 9607(a) of this title and that costs for which it seeks reimbursement are reasonable in light of the action required by the relevant order.

(D) A petitioner who is liable for response costs under section 9607(a) of this title may also recover its reasonable costs of response to the extent that it can demonstrate, on the administrative record, that the President's decision in selecting the response action ordered was arbitrary and capricious or was otherwise not in accordance with law. Reimbursement awarded under this subparagraph shall include all reasonable response costs incurred by the petitioner pursuant to the portions of the order found to be arbitrary and capricious or otherwise not in accordance with law.

(E) Reimbursement awarded by a court under subparagraph (C) or (D) may include appropriate costs, fees, and other expenses in accordance with subsections (a) and (d) of section 2412 of Title 28.

(c) **Guidelines for using imminent hazard, enforcement, and emergency response authorities; promulgation by Administrator of EPA, scope, etc.**

Within one hundred and eighty days after December 11, 1980, the Administrator of the Environmental Protection Agency shall, after consultation with the Attorney General, establish and publish guidelines for using the imminent hazard, enforcement, and emergency response authorities of this section and other existing statutes administered by the Administrator of the Environmental Protection Agency to effectuate the responsibilities and pow-

Attachment 3

Model Site Safety Plan for Chemical Safety Audits

SITE SAFETY PLAN FOR CHEMICAL SAFETY AUDITS

The OSHA Hazardous Waste Site Worker Standards (29 CFR 1910.120), the EPA Safety Manual, Chapter 9, and other EPA protocols require certain safety planning efforts prior to field activities. The following format is aligned with these requirements. Extensive training and certifications, and further planning in the form of a more extensive Site Safety Plan, may be required in addition to the following plan.

PROJECT: _____

Project Coordinator: _____ Date: _____

Branch Chief: _____ Date: _____

On Scene Coordinator or

Supervisor: _____ Date: _____

Health and Safety Manager

Approval: _____ Date: _____

DESCRIPTION OF ACTIVITY

If any of the following information is unavailable, mark "UA"; if covered in project plan, mark "PP."

Site Name: _____

Location and approximate size: _____

Description of the response activity and/or the job tasks to be performed:

Duration of the Planned Employee Activity: _____

Proposed Date of Beginning the Investigation: _____

Site Topography: _____

Site Accessibility by Air and Roads: _____

HAZARDOUS SUBSTANCES AND HEALTH HAZARDS INVOLVED OR
SUSPECTED AT THE SITE

Fill in any information that is known or suspected

<u>Areas of Concern</u>	<u>Chemical and Physical Properties</u>	<u>Identity of Substance and Precautions</u>
Explosivity:	_____	_____ _____ _____
Radioactivity:	_____	_____ _____ _____
Oxygen Deficiency: (e.g., Confined Spaces)	_____	_____ _____ _____
Toxic Gases:	_____	_____ _____ _____
Skin/Eye Contact Hazards:	_____	_____ _____ _____
Heat Stress:	_____	_____ _____ _____
Pathways from site for hazardous substance dispersion: _____ _____ _____ _____		

WORK PLAN INSTRUCTIONS

A. Recommended Level of Protection: A _____ B _____ C _____
Cartridge Type, if Level C: _____

CONTRACTOR PERSONNEL:

CONTRACTOR SAFETY CLOTHING/EQUIPMENT REQUIRED:

Have contractors received OSHA required training and certification?
(29 CFR 1910.120)

(If "yes," copy of training certificate(s) must be obtained from contractor)

B. Field Investigation and Decontamination Procedures:

Decontamination Procedures (contaminated protective clothing, instruments, equipment, etc.):

[illegible]

.....

[illegible][illegible]

Disposal Procedures (contaminated equipment, supplies, disposal items, wash-water, etc.): _____

EMERGENCY CONTACTS

Hospital Phone No.: _____

Hospital Location: _____

EMT/Ambulance Phone No.: _____

Police Phone No.: _____

Fire Assistance Phone No.: _____

Regional Health and Safety Manager: _____

Attachment 4

Sources of Information Concerning Hazardous Substance Releases

The **Accidental Release Information Program (ARIP)**. EPA established ARIP to promote safety initiatives by industry and to develop a national database on the causes of chemical accidents, but more importantly, to identify methods used to prevent recurrences. The data collected in ARIP are derived from questionnaires completed by selected facilities that have reported releases to the National Response Center (NRC), as required by law.

Facilities selected to receive an ARIP questionnaire have experienced a "triggered" release exhibiting one or more of the following characteristics:

- Release quantities in excess of a multiple of the CERCLA reportable quantity for the chemical involved;
- Releases resulting in deaths or injuries;
- Releases that are part of a trend of frequent releases from the same facility; or
- Releases involving extremely hazardous substances designated under SARA Title III.

State Emergency Response Commissions (SERCs) and Local Emergency Planning Committees (LEPCs). SERCs and LEPCs established under SARA Title III receive Section 304 reports detailing accidental releases of hazardous chemicals (those listed under the OSHA Hazard Communication Standard and CERCLA) and SERCs also received Section 313 reports recording annual releases, routine and accidental, of hazardous substances by manufacturing facilities.

The **National Response Center (NRC)**. The NRC receives notifications on accidental releases that are subject to Reportable Quantity requirements of CERCLA. The NRC has been notified of thousands of hazardous substance releases since 1978.

The **Emergency Response Notification System (ERNS)**. ERNS is a recent effort of the Agency to channel the state, regional, and NRC reports on releases of oil and hazardous substances into one central database. ERNS is used by EPA for enforcement tracking and program management purposes.

The **Environmental Protection Agency (EPA)**. Both the national and regional offices of EPA receive reports and notifications on accidental releases.

The **Acute Hazardous Events Data Base (AHE/DB)**. Designed by EPA, AHE/DB collects a representative sample of event reports from the above and other sources into a form that is more convenient for gaining perspective on accidental releases and drawing policy conclusions. Developed in 1985, it was recently updated and expanded to 6,300 records.

The **Section 305(b) Report to Congress on Emergency Systems**. Mandated by SARA Title III, the report was a three-stage process. Information on certain facilities with completed questionnaires is available. The report and backup information provide a good technical understanding for detecting, monitoring and preventing releases, as well as for public alert.

The **Federal Emergency Management Agency (FEMA)**. FEMA keeps a record of all incidents involving the participation of emergency management personnel.

The **Occupation Safety and Health Administration (OSHA)** and the **National Institute of Occupational Safety and Health (NIOSH)**. OSHA and NIOSH have records of accidents in the workplace.

U.S. Coast Guard Marine Safety Offices (MSO). Local MSOs regularly conduct inspections of waterfront facilities. These inspection reports are available from the respective MSO, and can provide useful facility information.

Attachment 5

Sample First Letter to Facility Owner/Operator

Dear (*Facility Owner/Operator*):

Through the records retained by the National Response Center pursuant to Section 103(a) of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980, as amended (CERCLA), the U.S. Environmental Protection Agency has identified your facility as a site where a reportable release of a CERCLA hazardous substance occurred. The EPA is currently conducting chemical safety audits of particular facilities identified through the Section 103(a) reporting system for the purpose of identifying technological and managerial mechanisms that might be implemented to prevent future threatened releases harmful to human health and the environment. The audit includes an on-site visit during which a review of equipment, procedures, training, and management techniques is conducted to learn about prevention of accidental chemical releases.

Due to a report filed by the (*facility name*) under Section 103(a) of CERCLA, (*facility name*) has been chosen as a potential candidate for an EPA chemical safety audit. The Agency is requesting your cooperation in an audit of your facility under the authorities of Sections 104(b) and 104(e) CERCLA, by (*names and affiliation of audit team*) on (*date*), or on a date convenient to you. Please be assured that the audit team will make every effort to minimize any interference with your plant operations during the actual safety audit.

If you wish to assert a business confidentiality claim for part or all of the information collected, such a claim must accompany the information when it is received by EPA, or it may be made available to the public without further notice to you. Information covered by a confidentiality claim will be disclosed by EPA only to the extent, and by means of the procedures, set forth in EPA regulations at 40 CFR Part 2. EPA has contracted with (*contractor name and contract number*) to obtain information pertinent to conducting the safety audit. (*Contractor name*) has been designated as an authorized representative of the Agency. Therefore, (*contractor name*) is subject to the provisions of Section 104(e) of CERCLA respecting confidentiality of methods or processes entitled to protection as trade secrets.

EPA would like to conduct this audit in a constructive and positive manner. The EPA solicits your prompt response to the above request. If you have any questions about the audit or the Chemical Safety Audit program, please contact (*regional contact*) for further information.

Sincerely,

Attachment 6

Sample Letter to Facility Owner/Operator who has not Responded or Consented to the Audit

Dear (Facility Owner/Operator):

Through the records retained by the National Response Center pursuant to Section 103(a) of the Comprehensive Environmental Response, Compensation and Liability Act of 1980, as amended (CERCLA), the U.S. Environmental Protection Agency has identified your facility as a site where a reportable release of a CERCLA hazardous substance occurred. The EPA is currently conducting chemical safety audits of particular facilities identified through the Section 103(a) reporting system for the purpose of identifying technological and managerial mechanisms that might be implemented to prevent future threatened releases harmful to human health and the environment. The (facility name) has been chosen for a chemical safety audit due to its reportable release(s) of (CERCLA hazardous substance(s)) on (date of release). The audit includes an on-site visit in which a review of equipment, procedures, training and management techniques is conducted to learn about prevention of accidental chemical releases. We wish to assure you that we will make every effort to minimize any interference with your plant operations during the course of the audit.

On (date) EPA sent you a letter requesting your voluntary cooperation in a chemical safety audit of your facility. [The Agency has not received a reply to that request.] [(By letter dated _____,) (/Through a telephone conversation on _____,) you indicated that you will not extend your voluntary cooperation to an audit of your facility.] You should be aware that Sections 104(b) and 104(e)(4)(A) of CERCLA specifically give EPA the right to access private property where there is a reasonable basis to believe that there has been or may be a release or threat of release of a hazardous substance or pollutant or contaminant. Failure to grant such access within _____ days of receipt of this letter, or adequately to justify such failure to grant such access, can result in EPA enforcing an order requesting entry pursuant to Section 104(e)(5) by seeking a warrant and/or penalties for noncompliance with the entry order. Section 104(e)(5)(B) of CERCLA permits EPA to seek the imposition of up to twenty-five thousand dollars (\$25,000) for each day that you fail to grant access to EPA. Please be further advised that provision of false, fictitious, or fraudulent statements or representations may subject you to criminal penalties under 18 U.S.C. Section 1001.

If you wish to assert a business confidentiality claim for part or all of the information collected, such a claim must accompany the information when it is received by EPA, or it may be made available to the public without further notice to you. Information covered by a confidentiality claim will be disclosed by EPA only to the extent and by means of the procedures set forth in EPA regulations at 40 CFR Part 2. EPA has contracted with (contractor name and contract number) to obtain information pertinent to conducting the safety audit. (Contractor name) has been designated as an authorized representative of the Agency. Therefore, (contractor name) is subject to the provisions of Section 104(e) of CERCLA respecting confidentiality of methods or processes entitled to protection as trade secrets.

Due to the legal ramifications of your failure to grant access, EPA strongly encourages you to give this matter your immediate attention and further consideration within the time specified. If you have any legal or technical questions relating to this matter, you may consult with the EPA prior to the time specified above. Please direct legal questions to (*Name of ORC Person*) of the Office of Regional Counsel at _____. Technical questions should be directed to (*Name of Program Person*), at the above address, or at _____.

Sincerely,

Attachment 7

Standard Report Disclaimer

The contents of this report reflect information concerning the (*facility name*) facility obtained during a U.S. Environmental Protection Agency chemical safety audit and from records provided by the (*facility name*) facility. The audit was conducted from (*audit dates*), and observations as presented in this report provide a snapshot of conditions existing at the facility during the audit time frame. They do not represent planned or anticipated changes proposed or on-going at the facility. The recommendations and other report observations contained in this report are not mandatory actions that the facility must implement. In addition, EPA makes no assurances that if implemented, the recommendations and other report observations contained in this report will prevent future chemical accidents, equipment failures, or unsafe management practices, and/or provide protection from a future enforcement action under any applicable law or regulation.

Attachment 8

Standard Language for Audit Report Introduction

The Chemical Safety Audit (CSA) program has evolved from the efforts of the U.S. Environmental Protection Agency (EPA) under the Chemical Accident Prevention (CAP) program. The primary objectives of the CAP program are to learn about the causes of accidental releases of hazardous substances and the means to prevent such releases from occurring, to promote industry initiatives in these areas, and to share activities with the community.

The Chemical Safety Audit program is part of this broad initiative, and has been designed to accomplish the following chemical accident prevention goals:

- Visit facilities handling hazardous substances to gather information on safety practices and technologies;
- Heighten awareness of the need for, and promote, chemical safety among facilities handling hazardous substances, as well as in communities where chemicals are located;
- Build cooperation among facilities, EPA, and other authorized parties by coordinating joint audits; and
- Establish a database for the assembly and distribution of chemical process safety management information obtained from the facility audits.

The audit consists of interviews with facility personnel, and on-site review of various aspects of facility operations related to the prevention of accidental chemical releases. CERCLA sections 104(b) and 104(e), as amended by SARA in 1986, provide authorities for entering a facility and accessing information. Specific topics addressed include:

- Awareness of chemical and process hazards;
- Process characteristics;
- Emergency planning and preparedness activities;
- Hazard evaluation and release modelling efforts;
- Release detection and monitoring techniques;
- Training of operators and emergency response personnel;
- Facility and corporate management structure;
- Preventive maintenance and inspection programs; and
- Community notification mechanisms and techniques.

This report contains observations and conclusions and recommendations from an audit conducted at (*facility name, city, and state*) from (*audit dates*). This report identifies and characterizes the strengths of specific chemical accident prevention program areas to allow the elements of particularly effective programs to be recognized. Copies of the report are provided to the facility so that weak and strong program areas may be recognized.

Attachment 9

Documentation Pertaining to the Processes and Operations Using Hazardous Substances

The issues contained in sections 6.2.1 and 6.2.2 of the CSA protocol, *Overview of Processing Steps and Operating Procedures* and *General Description of Process Equipment*, will require members of the audit team to review processing and operating information. The team should review facility documentation on the equipment and operating procedures relevant to the audit. Before examining current practices, the audit team may want to review available technical documentation supporting the original selection of technology, process chemistry, equipment, and operating parameters for the process(es) under study. Typical documentation available for current operations include Process Flow Diagrams (PFDs) and Piping and Instrumentation Diagrams (PIDs). The following questions can provide a framework for your evaluation of these documents:

- Does the facility have documentation on the design and operating parameters of the equipment and processes using the substance(s) of interest?
- Is the documentation for the process(es) complete, accurate, and legible?
- Are symbols used uniformly?
- Are items such as the location and sizes of nozzles for connection of process lines, utility tie-ins, relief devices, controls, drains, vents, and blinds included?
- Do pieces of equipment have assigned numbers and are descriptions provided?
- Are the equipment specifications and operating parameters (e.g., dimensions, capacity, surface area, temperatures, pressures) specified?
- Are equipment spares shown?
- For piping, are the items such as rating, diameter, fluid flow direction, insulation and tracing requirements, and sloping requirements for expansion shown?
- For instrumentation, are items such as control parameter, indicating and recording functions, transmitter, signal type, control valve size, and actuator type shown?

Other issues to keep in mind when examining process documentation include materials of construction; electrical area classification; design of relief, safety, and ventilation systems; relevant design codes and standards; and material and energy balances.

PIDs indicate whether or not the crucial operating parameters are being monitored in order for the operator to be able to respond to upsets in a timely manner. Therefore, the team should review a PID for the following concerns: monitoring of operating parameters, provisions for automatic shutdown, presence of alarm systems, interlock systems, overpressure protection, disposal method of relief stream, and similar information. The audit team may want to compare a portion of the PID to the systems and equipment in existence at the facility to verify their accuracy.

Attachment 10

Descriptions of Standard Operating Procedure Manuals

Section 7.2.1 of the CSA protocol, *Standard Operating Procedures*, lists several types of SOP manuals that should be reviewed, as relevant, by the audit team. In general, the audit team should consider whether existing facility SOPs are complete -- do they address initial and post-shutdown startups, normal operations, temporary and emergency operations, normal and emergency shutdowns, and maintenance. The following descriptions provide a summary of the type of information that facility SOP manuals typically contain.

Supervisory Operating Manual

- Feed and product specifications;
- PFDs; PIDs; MSDSs;
- Process parameters;
- Intermediate stream normal operating guidelines;
- List of alarms and interlocks;
- Equipment and instrumentation settings;
- Narrative description of start-up;
- Testing practices;
- Shutdown; and
- Emergency situations.

Operating Procedures Manual

- Detailed valve-by-valve procedures for all operating tasks;
- Schematic drawings;
- Safety instructions; and
- Equipment and systems.

Safety Procedures Manual

- Safety systems and equipment;
- Safety procedures; and
- Instructions.

In addition to comprehensiveness, the audit team should determine whether the SOP manuals accurately reflect current equipment and current practices and whether they are understood and implemented by operations personnel. Finally, the audit team should determine whether the manuals are formally evaluated on a regular basis, whether both operations and management personnel participate in the review and revision of SOPs, and how information on such changes is provided to operations and supervisory personnel through training and drills.

Beyond the manuals listed above, there are a variety of other procedural documents (e.g., operating logs, shift turnover procedures, and maintenance guidelines) that the audit team may want to examine, depending on the focus of the audit. Safety, health, and accident prevention topics that can be investigated through these sources include overtime practices, emergency callout procedures, procedures for reporting unusual occurrences, and consistency of equipment handling procedures for maintenance and operations personnel.

Attachment 11

Blank CSA Report Profile

CHEMICAL SAFETY AUDIT PROFILE

Facility Name:

Facility Location:

Date(s) Audit Conducted:

Description of Facility:

SIC Code(s):

Location:

Products manufactured,
produced, or distributed:

Proximity to
sensitive populations:

Reason for Facility Selection:

ARIP Reports:

Focus of Audit:

Hazardous Substances(s)
Examined:

Physical Area(s) Examined:

Storage and Handling

- Storage Systems
- Shipping/Receiving
- Material Transfer

Process Area(s)

Summary of Audit Findings and Recommendations:

Conclusions:

Facility Background Information

-
-
-
-

Chemical Hazards

-
-
-
-

Process Information

-
-
-
-

Chemical Accident Prevention

-
-
-
-

Accidental Release Incident Investigation

-
-
-
-

Facility Emergency Preparedness and Planning Activities

-
-
-
-

Community and Facility Emergency Response Planning Activities

-
-
-
-

Public Alert and Notification Procedures

-
-
-
-

Recommendations:

Facility Background Information

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-
-
-

Chemical Hazards

-
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-

Process Information

-
-
-
-

Chemical Accident Prevention

-
-
-
-

Accidental Release Incident Investigation

-
-
-
-

Facility Emergency Preparedness and Planning Activities

-
-
-
-

Community and Facility Emergency Response Planning Activities

-
-
-
-

Public Alert and Notification Procedures

-
-
-
-

Audit Team Member Composition:

Name and Title
Affiliation
Area of Responsibility
Expertise

Name and Title
Affiliation
Area of Responsibility
Expertise

Name and Title
Affiliation
Area of Responsibility
Expertise

Name and Title
Affiliation
Area of Responsibility
Expertise

Name and Title
Affiliation
Area of Responsibility
Expertise

Name and Title
Affiliation
Area of Responsibility
Expertise

Name and Title
Affiliation
Area of Responsibility
Expertise

Follow-up Activities:

By the facility:

By the Regional office:

By State and local authorities:

Regional Contact:

Date:

Attachment 12

Annotated CSA Report Profile

CHEMICAL SAFETY AUDIT PROFILE

Facility Name: [provide full name of facility as well as any corporate affiliation]

Facility Location: [list city, state, and region]

Date(s) Audit Conducted: [list actual days audit team was on site at facility]

Description of Facility:

SIC Code(s): [provide four-digit SIC code]

Location: [describe nature of surrounding area (e.g., commercial, industrial, rural, residential, urban) and indicate direction and distance to nearest major city]

Products manufactured, produced, or distributed: [list final products and intended uses]

Proximity to sensitive populations: [indicate direction and distance to schools, hospitals, day care centers, senior centers, parks, lakes, wetlands, and other sensitive environments]

Reason for Facility Selection: [list all reasons, including past releases, ARIP questionnaires, requests from state and local officials, regional initiatives, interest from facility, public concern, chemical(s), process(es), or system(s) of interest]

ARIP Reports: [list release date and substance released]

Focus of Audit:

Hazardous Substances(s)

Examined:

[list only CERCLA hazardous substances or Title III extremely hazardous substances examined and provide Chemical Abstract Service (CAS) number]

Physical Area(s) Examined:

Storage and Handling

- **Storage Systems**

[describe all storage systems examined (e.g., rail cars, tanks, containers, cylinders), including design, capacity, material of construction, and length of storage]

- **Shipping/Receiving**

[describe all shipping and receiving systems examined (e.g., rail car, tank truck, and barge loading/unloading areas, pipelines), including frequency of delivery/shipment, design, capacity, and general loading/unloading procedures]

- **Material Transfer**

[describe all material transfer systems examined (e.g., pipelines, conveyor belts, fork lifts, manual), including design, material of construction, capacity, and general transfer procedures]

Process Area(s)

[describe each stage in all process(es) examined involving the hazardous substances (e.g., primary and secondary manufacturing, recycling and reuse, waste and waste water treatment and disposal, power generation), including substances and equipment involved and a general description of each step in the process]

Summary of Audit Findings and Recommendations:

Conclusions:

[state observations and concerns on facility policies and practices in a factual manner that refrains from judgments of adequacy or inadequacy, and ensure that any concerns have been addressed appropriately in the recommendations section.]

Facility Background Information

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-
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Chemical Hazards

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-

Process Information

-
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-
-

Chemical Accident Prevention

-
-
-
-

Accidental Release Incident Investigation

-
-
-
-

Facility Emergency Preparedness and Planning Activities

-
-
-
-

Community and Facility Emergency Response Planning Activities

-
-
-
-

Public Alert and Notification Procedures

-
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-
-

Recommendations:

[clearly state recommendations for facility policies and practices (that are both practical and technologically feasible at the facility) in a manner that reflects their non-mandatory nature, as well as the observations and concerns outlined in the conclusions section.]

Facility Background Information

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-
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Chemical Hazards

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-
-

Process Information

-
-
-
-

Chemical Accident Prevention

-
-
-
-

Accidental Release Incident Investigation

-
-
-
-

Facility Emergency Preparedness and Planning Activities

-
-
-
-

Community and Facility Emergency Response Planning Activities

-
-
-
-

Public Alert and Notification Procedures

-
-
-
-

Audit Team Member Composition:

[list audit team members in the following order: US EPA team leader, other US EPA personnel, AARP enrollees, TAT members, representatives from other federal agencies; and then state, tribal, and local officials]

Name and Title	[list the full name and title of the auditor]
----------------	---

Affiliation	[indicate the federal, state, tribal, or local government organization that the auditor is representing (e.g., US EPA regional office; Technical Assistance Team -- company name; state department of environmental protection; county health department)]
-------------	--

Area of Responsibility	[indicate the general subject matter(s) with which the auditor was involved (e.g., equipment and process(es), training, off-site impacts, occupational health, security, emergency planning, observer)]
------------------------	---

Expertise [characterize the education, training, and/or professional background of the auditor (e.g., chemical engineer, public health officer, hazardous waste specialist, emergency responder, emergency planner)]

Name and Title
Affiliation
Area of Responsibility
Expertise

Name and Title
Affiliation
Area of Responsibility
Expertise

Name and Title
Affiliation
Area of Responsibility
Expertise

Name and Title
Affiliation
Area of Responsibility
Expertise

Name and Title
Affiliation
Area of Responsibility
Expertise

Name and Title
Affiliation
Area of Responsibility
Expertise

Follow-up Activities:

By the facility:

[as appropriate, discuss short and long term plans of facility to address issues/implement recommendations raised during the audit]

By the Regional office:

[as appropriate, discuss short and long term plans to follow up with facility on issues and recommendations raised during the audit]

By State and local authorities:

[as appropriate, discuss follow up activities related to issues and recommendations raised during the audit]

Regional Contact: [list contact for further information]

Date: [indicate date that profile was submitted]

OXYGEN MONITORS, COMBUSTIBLE GAS INDICATORS, AND SPECIFIC CHEMICAL MONITORS

PERFORMANCE OBJECTIVES

At the end of this lesson, participants will be able to:

- Identify the purpose for oxygen monitoring
- List the four factors that can affect oxygen monitor response
- Identify the purpose for combustible gas monitoring
- List the four factors that can affect combustible gas indicator response
- Identify the purpose of toxic atmosphere monitoring
- List three types of toxic atmosphere monitors
- List four types of specific chemical monitors
- List four factors that can affect the response of specific chemical monitors.

NOTES

OXYGEN MONITORS, COMBUSTIBLE GAS INDICATORS, AND SPECIFIC CHEMICAL MONITORS

HAZARDS

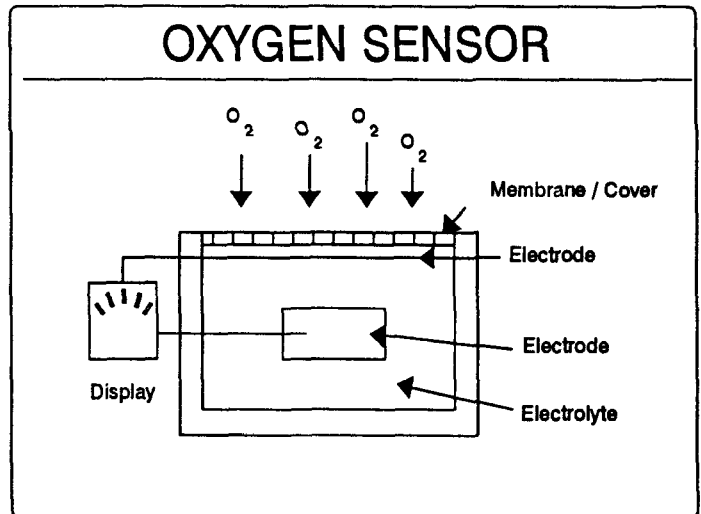
- Oxygen-deficient atmospheres
- Combustible/explosive atmospheres
- Toxic atmospheres
- Radiation

OXYGEN MONITORING

Aid in determining:

- Type of respirator needed
- Flammability risk
- Sufficient oxygen for combustible gas indicators (CGIs)
- Presence of contaminants

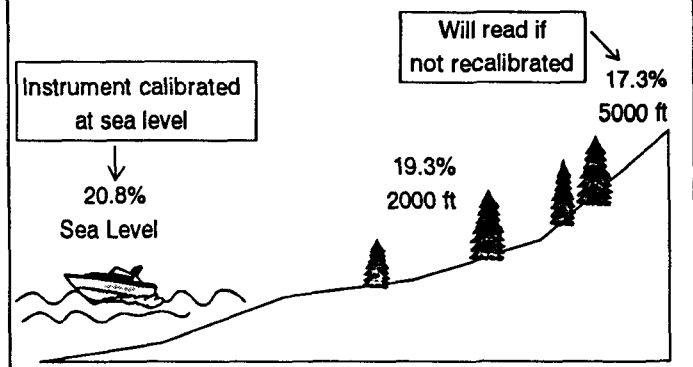
NOTES



OXYGEN MONITORS Considerations

- Life span
- Operating temperature
- Interfering gases
- Atmospheric pressure

ALTITUDE/OXYGEN METER READING

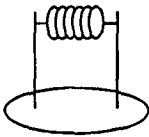


NOTES

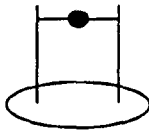
FLAMMABLE ATMOSPHERE MONITORING

- Used to determine risk of fire or explosion
- CGI readings are indicative of relatively high concentrations of contaminants

COMBUSTIBLE GAS INDICATORS Catalytic Sensors

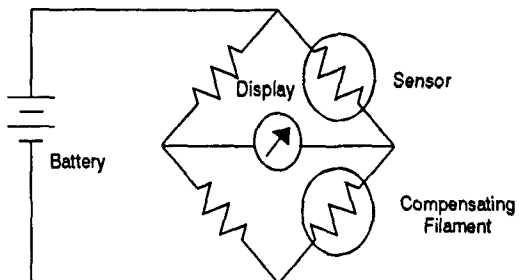


Filament



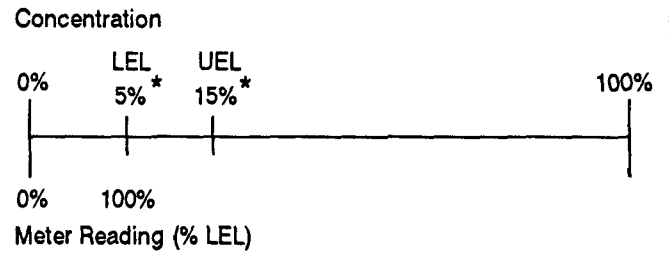
Bead

COMBUSTIBLE GAS INDICATORS Wheatstone Bridge Circuit



NOTES

COMBUSTIBLE GAS INDICATORS Instrument Reading vs Concentration

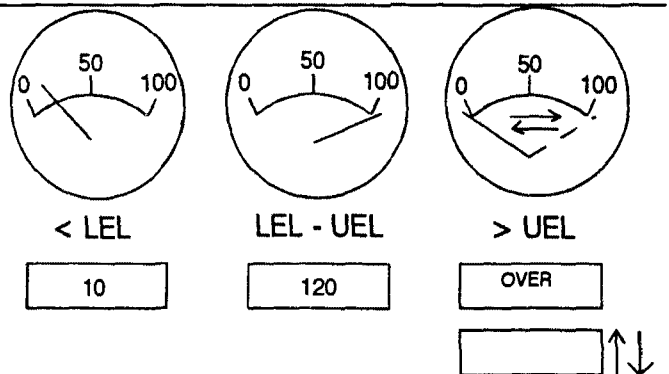


Note: * = methane

LEL = lower explosive limit

UEL = upper explosive limit

COMBUSTIBLE GAS INDICATORS Readouts



COMPARISON OF LEL READINGS WITH ACTUAL CONCENTRATIONS

Hexane LEL = 1.1%

For an instrument calibrated to hexane measuring hexane:

100%	= 1.1%	(11,000 ppm)
50%	= 0.55%	(5,500 ppm)
25%	= 0.275%	(2,750 ppm)
10%	= 0.11%	(1,100 ppm)
1%	= 0.011%	(110 ppm)

NOTES

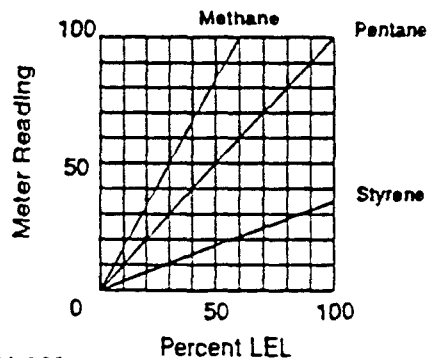
COMBUSTIBLE GAS INDICATORS Readout Ranges

- "Normal" units
 - 0 - 100% LEL
 - 0 - 10% LEL
- "Supersensitive" units
 - Parts per million (ppm)
 - Example: TLV Sniffer,
Gastech Model 1314

COMBUSTIBLE GAS INDICATORS Considerations

- Oxygen requirements
- Contaminants that foul sensor
- Temperature
- Relative response

COMBUSTIBLE GAS INDICATORS Relative Response Curves



Source: MSA 260

NOTES

TOXIC ATMOSPHERE MONITORING

The purpose of monitoring is to:

- Identify chemicals and their concentrations
- Evaluate worker/public exposures
- Evaluate protective equipment selection
- Help develop exposure controls

TOXIC ATMOSPHERE MONITORS

- Specific chemical monitors
- Total vapor survey monitors
- Gas chromatographs
- Aerosol monitors

SPECIFIC CHEMICAL MONITORS

- Designed to respond to a specific chemical
- Common types include
 - Electrochemical
 - Metal-oxide semiconductor (MOS)
 - Colorimetric indicators
 - Mercury detectors

NOTES

METAL-OXIDE SEMICONDUCTOR (MOS)

- Metal-oxide coating on a ceramic substrate wrapped around a wire
- Contaminant alters conductivity by removing oxygen
- Change in current is proportional to the amount of contaminant present
- Also called "solid-state" sensor

MOS Considerations

- Interferences
- Saturation
- Temperature
- Minimum oxygen requirements

COLORIMETRIC INDICATORS

Contaminant reacts with a chemical on a tape, badge, or tube and causes a color change

NOTES

COLORIMETRIC INDICATORS Considerations

- Interferences
- Humidity
- Temperature

MERCURY DETECTORS

- Ultraviolet light absorption
 - Mercury vapor absorbs a specific wavelength of light
- Gold film
 - Mercury reacts with film and changes the electrical resistance of the film

MERCURY DETECTORS Considerations

- Ultraviolet light
 - Interferences
 - Humidity
- Gold film
 - Factory calibration
 - AC power needed to "clean"

OXYGEN MONITORS, COMBUSTIBLE GAS INDICATORS, AND SPECIFIC CHEMICAL MONITORS

INTRODUCTION

Many hazards may be present when responding to hazardous materials spills or uncontrolled waste sites. These include oxygen-deficient atmospheres, combustible/explosive atmospheres, toxic atmospheres, and radiation. There are several types of instrumentation for detecting hazardous atmospheres. This section will discuss oxygen monitors, combustible gas indicators (CGIs), and monitors for specific chemicals.

OXYGEN MONITORS

Oxygen monitors are used to evaluate an atmosphere for:

- Oxygen content for respiratory purposes. Normal air contains 20.8% oxygen. Generally, if the oxygen content decreases below 19.5%, it is considered oxygen-deficient and special respiratory protection is needed.
- Increased risk of combustion. Generally, concentrations above 25% are considered oxygen enriched and increase the risk of combustion.
- Use of other instruments. Some instruments require sufficient oxygen for operation. For example, CGIs do not give reliable results at oxygen concentrations below 10%. Also, the inherent safety approvals for instruments are for normal atmospheres and not for oxygen-enriched ones.
- The presence of contaminants. A decrease in oxygen content can be due to the consumption (by combustion or a reaction such as rusting) of oxygen or the displacement of air by a chemical. If it is due to consumption, then the concern is the lack of oxygen. If it is due to displacement, then there is something present that could be flammable or toxic. Because oxygen makes up only 20.8% of air, a 1% drop in oxygen means that about 5% air (air being 1 part oxygen and 4 parts nitrogen) has been displaced. This means that 5% or 50,000 ppm (1% = 10,000 ppm) of "something" could be there.

Most indicators have meters that display the oxygen concentration from 0 to 25%. There are also oxygen monitors available that measure concentrations from 0 to 5% and from 0 to 100%. The most useful range for hazardous material response is the 0–25% oxygen content readout because decisions involving air-supplying respirators and the use of CGIs fall into this range.

The oxygen sensor can be on the outside (external) or inside (internal) of the instrument. Internal sensors need a pump—battery operated or hand operated—to draw a sample to it. Units that combine O₂ meters and CGIs into one instrument are available from many manufacturers. Also, flashing and audible alarms can be found on many instruments. These alarms go off at a preset oxygen

concentration to alert the users even if they are not watching the meter. A list of manufacturers of oxygen monitors is found in this manual under *Manufacturers and Suppliers of Air Monitoring Equipment*.

Principle of Operation

Oxygen monitors use an electrochemical sensor to determine the oxygen concentration in air. A typical sensor consists of two electrodes, a housing containing a basic electrolytic solution, and a semipermeable Teflon® membrane (Figure 1).

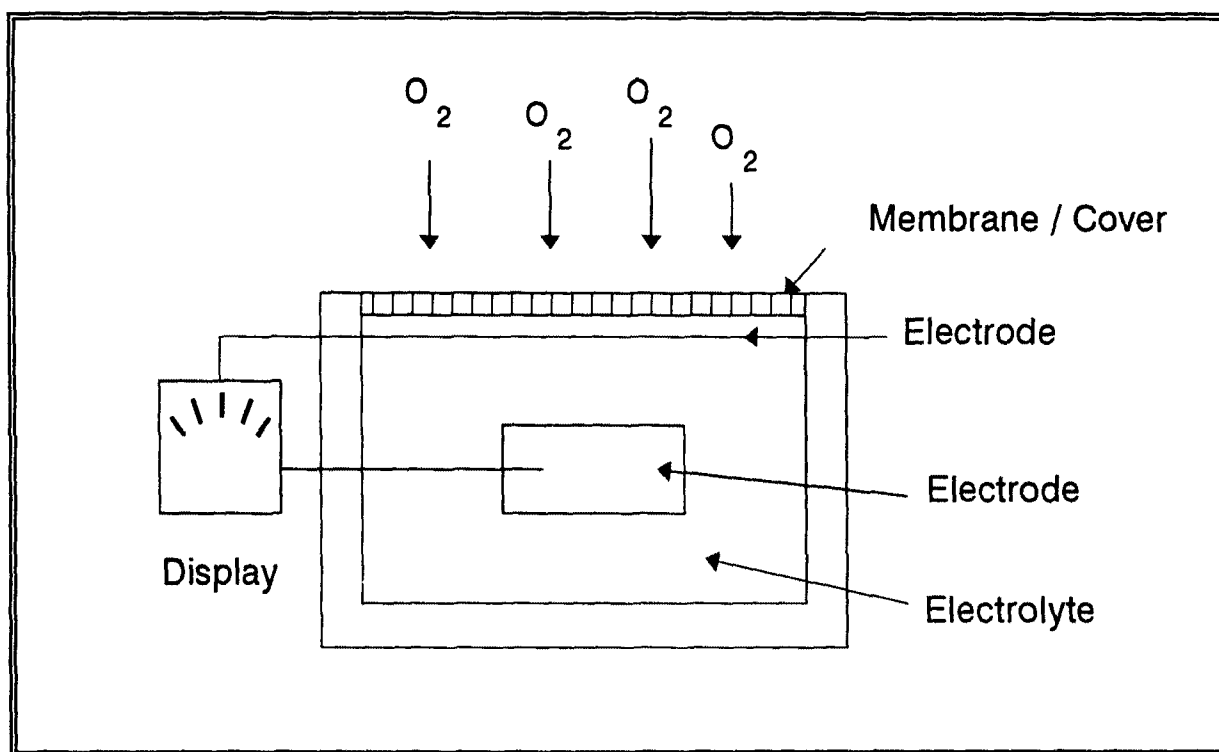


FIGURE 1. SCHEMATIC OF OXYGEN SENSOR

Source: *Atmospheric Monitoring for Employee Safety*, BioMarine Industries Inc.

Oxygen molecules (O_2) diffuse through the membrane into the solution. Reactions between the oxygen, the solution, and the electrodes produce a minute electrical current proportional to the oxygen content. The current passes through an electronic circuit which amplifies the signal. The resulting signal is shown as a needle deflection on a meter or as a digital reading.

In some units, air is drawn into the oxygen detector with an aspirator bulb or pump; in other units, the ambient air is allowed to diffuse to the sensor.

Limitations and Considerations

The operation of oxygen monitors depends on the absolute atmospheric pressure. The concentration of atmospheric oxygen is a function of the atmospheric pressure at a given altitude. Whereas the actual percentage of oxygen does not change with altitude, at sea level the weight of the atmosphere above is greater, and more O₂ molecules (and the other components of air) are compressed into a given volume than at higher elevations. As elevation increases, this compression decreases, resulting in fewer air molecules being "squeezed" into a given volume. Consequently, an O₂ indicator calibrated at sea level and operated at an altitude of several thousand feet will falsely indicate an oxygen-deficient atmosphere because less oxygen is being "pushed" into the sensor. Therefore, it is necessary to calibrate at the altitude the instrument is used.

The reaction that produces the current in the sensor is nonreversible. Thus, once the sensor is exposed to oxygen, it begins to wear out. The normal life span of a sensor is 6 months to 1 year. Sensors are shipped in sealed packages that have been purged with nitrogen. The packet should not be opened until the sensor is to be used. Storing the sensor in an oxygen absent atmosphere after opening the package can prolong the sensor life, but may not be practical.

High concentrations of carbon dioxide (CO₂) may shorten the useful life of the oxygen sensor. As a general rule, the unit can be used in atmospheres greater than 0.5% CO₂ only with frequent replacing or rejuvenating of the sensor. Lifetime in a normal atmosphere (0.04% CO₂) can be from 6 months to 1 year depending on the manufacturer's design. The service life of one sensor is 100 days in 1% CO₂ and 50 days in 5% CO₂.

Strong oxidizing chemicals, like ozone and chlorine, can cause increased readings and indicate high or normal O₂ content when the actual content is normal or even low.

Temperature can affect the response of oxygen indicators. The normal operating range for them is between 32°F and 120°F. Between 0°F and 32°F the response of the unit is slower. Below 0°F the solution may freeze and damage the sensor. High temperature can also shorten the sensor life. The instrument should be calibrated at the temperature at which it will be used.

COMBUSTIBLE GAS INDICATORS

CGIs measure the concentration of a flammable vapor or gas in air, indicating the results as a percentage of the lower explosive limit (LEL) of the calibration gas. The LEL (or LFL - lower flammable limit) of a combustible gas or vapor is the minimum concentration of the material in air which will propagate flame on contact with an ignition source. The upper explosive limit (UEL) is the maximum concentration. Below the LEL there is insufficient fuel to support combustion. Above the UEL, the mixture is too "rich" to support combustion, so ignition is not possible. Concentrations between the LEL and UEL are considered flammable.

CGIs are available in many styles and configurations. The combustible gas sensor can be on the outside (external) or inside (internal) of the instrument. Internal sensors need a pump—battery operated or hand operated—to draw a sample to it. Many units are "combination meters." This means they have an O₂ meter and a CGI (and sometimes one or two specific gas indicators)

combined in the same instrument. Flashing and audible alarms are options on many units. The alarms go off at a preset concentration to warn the instrument operator of potentially hazardous concentrations. Other options such as longer sampling lines, moisture traps, and dust filters are also available. Manufacturers of CGIs are listed in *Manufacturers and Suppliers of Air Monitoring Equipment*.

Principle of Operation

CGIs use a combustion chamber containing a filament that combusts the flammable gas. To facilitate combustion, the filament is heated or is coated with a catalyst (like platinum or palladium), or both. The filament is part of a balanced resistor circuit called a Wheatstone bridge (Figure 2). The hot filament combusts the gas on the immediate surface of the element, thus raising the temperature of the filament. As the temperature of the filament increases, so does its resistance. This change in resistance causes an imbalance in the Wheatstone bridge. This is measured as the ratio of combustible vapor present compared to the total required to reach the LEL. For example, if the meter reads 50% (or 0.5, depending upon the readout), this means that 50% of the concentration of combustible gas needed to reach a flammable or combustible situation is present. If the LEL for the gas is 5%, then the meter would be indicating that a 2.5% concentration is present. Thus, the typical meter indicates concentration up to the LEL of the gas (Figure 3a).

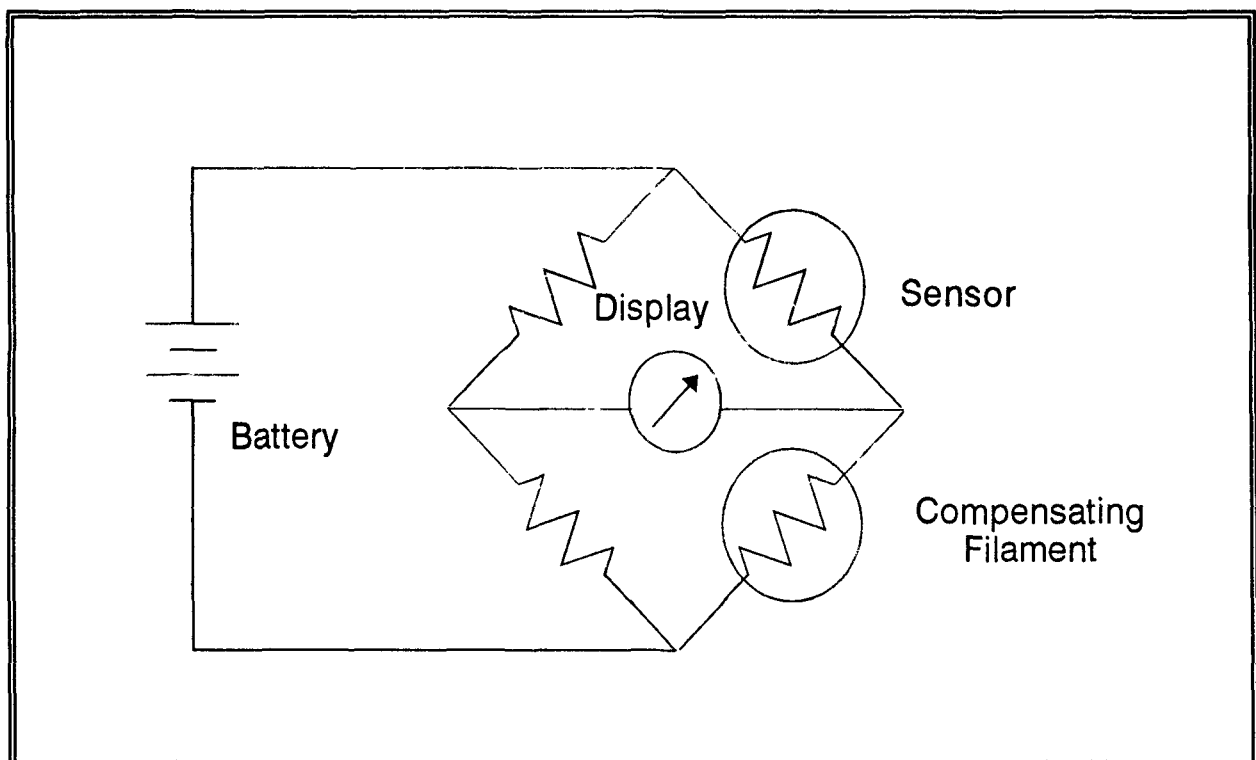


FIGURE 2. WHEATSTONE BRIDGE CIRCUIT

Source: *Atmospheric Monitoring for Employee Safety*, BioMarine Industries Inc.

If a concentration greater than the LEL and lower than the UEL is present, then the meter needle will stay beyond the 100% (1.0) level on the meter (Figure 3b). This indicates that the ambient atmosphere is readily combustible. When the atmosphere has a gas concentration above the UEL, the meter needle may rise above the 100% (1.0) mark and then return to zero (Figure 3c). This occurs because the gas mixture in the combustion cell is too rich to burn. This permits the filament to conduct a current just as if the atmosphere contained no combustibles at all. Some instruments have a lock mechanism that prevents the needle from returning to zero when it has reached 100%. This mechanism must be reset in an atmosphere below the LEL.

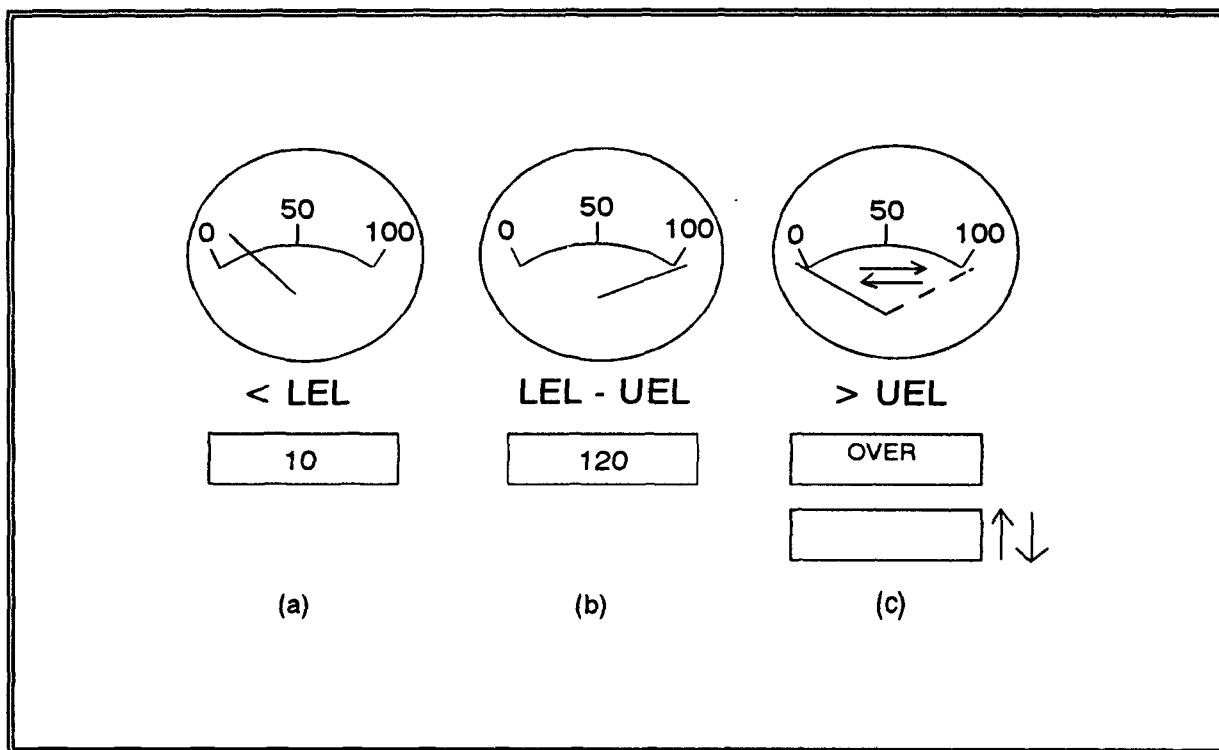


FIGURE 3. COMPARISON OF METER READINGS TO COMBUSTIBLE GAS CONCENTRATIONS

Limitations and Considerations

The instruments are intended for use only in normal oxygen atmospheres. Oxygen-deficient atmospheres will produce lowered readings. Also, the safety guards that prevent the combustion source from igniting a flammable atmosphere are not designed to operate in an oxygen-enriched atmosphere.

Organic lead vapors (e.g., leaded gasoline), sulfur compounds, and silicone compounds will foul the filament. Acid gases (e.g., hydrogen chloride and hydrogen fluoride) can corrode the filament. Most units have an optional filter that protects the sensor from leaded vapors.

The response of the instrument is temperature dependent. If the temperature at which the instrument is zeroed differs from the sample temperature, the accuracy of the reading is affected. Hotter temperatures raise the temperature of the filament and produce a higher than actual reading. Cooler temperatures will reduce the reading. The instrument should be calibrated and zeroed at the same temperature that a reading will be taken. Some instruments have a compensating filament (**Figure 2**). This filament is similar to the sensor and is exposed to the same atmosphere, but it does not combust the atmosphere. It compensates for any temperature changes not caused by the combustible gas.

There is no differentiation between petroleum vapors and combustible gases. If the flammability of the combined vapors and gases in an atmosphere is the concern, this is not a problem. However, if the instrument is being used to detect the presence of a released flammable liquid—like gasoline—in a sewer system where methane may be present, the operator cannot tell whether the reading is the contaminant or the methane. A prefilter can be used to remove the vapors, but it will not remove the methane. Thus, if readings are made with and without the filter, the user can compare the readings and can conclude that differences in the values indicate that a petroleum vapor (i.e., the contaminant) is present.

Relative response is also a concern. If the CGI is used to monitor a gas/vapor that the unit is not calibrated to, it can give inaccurate results. **Figure 4** illustrates the effect of relative response.

TOXIC ATMOSPHERE MONITORS

Along with oxygen concentration and flammable gases or vapors, there is also a concern about chemicals present at toxic concentrations. This usually involves measurements at concentrations lower than what would be indicated by oxygen indicators or CGIs. There is a need to determine whether toxic chemicals are present and identify them so the environmental concentration can be compared to exposure guidelines. Toxic atmosphere monitoring is done to:

- Identify airborne chemicals and their concentrations
- Evaluate the exposure of workers and the public
- Evaluate the need for and type of personal protective equipment
- Develop controls for exposure in the form of engineered safeguards, work practices, safety plans, and work zones.

Several different groups of instruments can be used for these functions. In this manual the following types will be discussed:

- *Specific chemical monitors* are instruments designed to respond to a specific chemical. Common types include instruments that use electrochemical cells or metal-oxide semiconductors (MOS), colorimetric indicators, and mercury detectors.

- *Total vapor survey meters* have detectors (e.g., photoionization detector [PID] or flame ionization detector [FID]) that respond to a variety of chemicals. Additional information can be found in *Total Vapor Survey Instruments*.
- *Gas chromatographs* are used to help identify what chemicals are present in the atmosphere. Additional information is available in *Introduction to Gas Chromatography*.

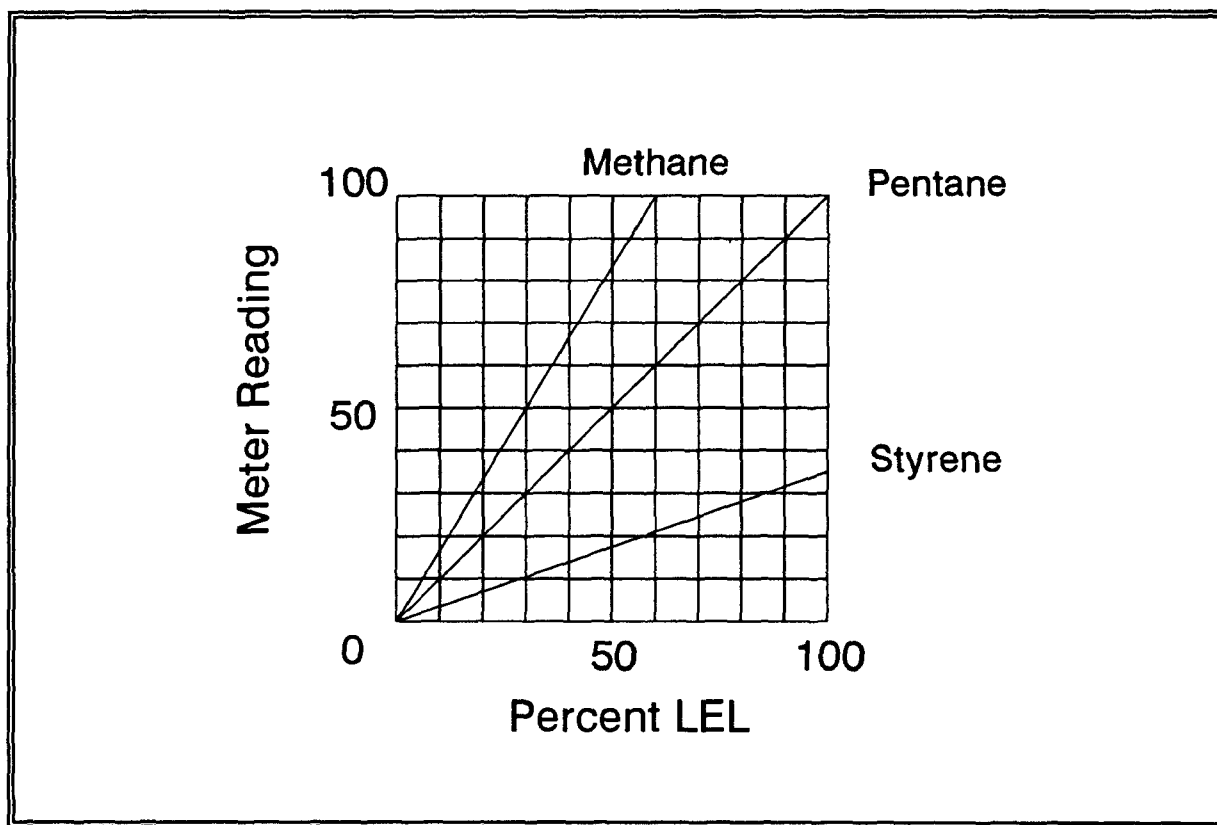


FIGURE 4. EXAMPLES OF RELATIVE RESPONSE CURVES FOR MSA MODEL 260

Source: *Portable Gas Indicator, Model 250 and 260, Response Curves*, Mine Safety Appliances Company, Pittsburgh, PA.

SPECIFIC CHEMICAL MONITORS

Electrochemical Cells

Electrochemical cells (Figure 1) contain a chemical solution and two or more electrodes. The chemical reacts with the solution or the electrodes. The reaction can be a generation of electrical current or a change in conductivity of the solution. The change in signal is expressed as a needle

movement or a digital response on a meter. The selectivity of the sensor depends on the selection of the chemical solution and the electrodes.

In addition to the previously mentioned oxygen monitors (**Figure 1**), there are electrochemical sensors for ammonia, carbon monoxide, carbon dioxide, chlorine, hydrogen chloride, hydrogen cyanide, and hydrogen sulfide. Examples of these instruments are Compur's **Monitox®** Personal Monitor Alarms, MDA's **MSTox 8600** series, and National Draeger's **PAC** series of personal monitors.

Limitations and Considerations

Like the oxygen sensor, these electrochemical sensors also can wear out and are affected by temperature and humidity.

Electrochemical cells are also affected by interferences. For example, many of the carbon monoxide sensors will also respond to hydrogen sulfide. In fact, one manufacturer uses the same sensor for both carbon monoxide and hydrogen sulfide detectors. The user must inform the instrument which chemical is being monitored so the readout is in the proper units.

Metal-Oxide Semiconductors

MOS detectors, also called solid-state sensors, consist of a metal-oxide film coating on heated ceramic substrate fused or wrapped around a platinum wire coil. When a gas comes in contact with the metal oxide, it replaces oxygen in the oxide and alters the conductivity of the semiconductor. The change in conductivity can be expressed in a meter readout. The substrate is heated to give a constant baseline as oxygen in the air can combine with the oxide. Selectivity can be determined by selecting specific metal oxides and/or using specific temperatures from the heater to prevent chemicals from reacting.

There are MOS detectors for ammonia, carbon monoxide, hydrogen chloride, hydrogen cyanide, hydrogen sulfide, methyl chloride, nitrogen oxides, and sulfur dioxide. Examples of instruments that use an MOS to detect specific toxic compounds are the Enmet **Tritechtor®** and Biosystem's **Model 100** series.

Even though the choice of metal oxide and sensor temperature can make the detector somewhat selective, interferences are a major problem.

Because the sensor reaction is based on presence (or absence) of oxygen in the metal-oxide film, factors that affect oxygen concentration affect meter response. The sensor needs a minimum 14% ambient oxygen for operation. High concentrations can saturate the sensor, causing a slow recovery.

A minimum of 10% humidity is need for some sensors (check the manufacturer's specifications).

Colorimetric Indicators

Colorimetric indicators use a chemical to react with the contaminant to produce a color change. The chemical can be impregnated on a tape or a badge or put inside a glass tube. The color change can be read by the human eye or by a spectrophotometer to determine the concentration of the contaminant.

The chemicals are not always specific and can be affected by interfering chemicals. Humidity can act as an interference by producing a reaction. Cold temperatures can slow the chemical reaction. Hot temperatures may also cause the chemicals to indicate a reaction.

Examples of colorimetric indicators are the Envirometrics, Inc. **ACT™ cards** (badges), MDA Scientific's **7100 Series** (tape), and Draeger detector tubes.

Mercury Detectors

Mercury detectors use either ultraviolet light absorption or a gold film detector. Mercury vapor absorbs a certain wavelength of ultraviolet light. The instrument draws a sample into a chamber and exposes it to the ultraviolet light source. The concentration of mercury vapor is measured by the amount of light absorbed.

Some organic chemicals can absorb the ultraviolet light and act as an interference. Water vapor also absorbs ultraviolet light, but can be adjusted for if the instrument is zeroed in the same humidity as the sample area.

The gold film detector has a gold film as part of a circuit. Mercury reacts with the gold and changes the resistance of the film. The change in resistance is used to determine concentration.

Because most operators do not have a mercury vapor standard, the gold film detector must be factory calibrated. After long exposures or high concentrations, the film needs to be "cleaned." This requires heating the film and using an AC power source.

An example of an ultraviolet absorption instrument is the Bacharach **Model MV-2**. An example of a gold film instrument is the Jerome Instruments **Model 411**.

CONCLUSION

Many hazards can be present at a hazardous materials operation. Instruments are available for determining the presence of hazardous situations like combustible atmospheres, oxygen-deficient atmospheres, and toxic atmospheres. The instruments discussed in this section can only identify certain hazardous situations and should be selected and used accordingly. Additional information on identifying and evaluating toxic atmospheres will be discussed in the following sections.

TOTAL VAPOR SURVEY INSTRUMENTS

PERFORMANCE OBJECTIVES

At the end of this lesson, participants will be able to:

- Explain the principle of detection for the PID, FID, supersensitive CGI, and metal-oxide semiconductor (MOS)
- Determine whether a chemical can be detected by photoionization, given the ionization potential of the chemical and the lamp energy of the photoionization detector
- Identify three considerations when using a PID
- Identify three considerations when using a FID
- Identify three consideration when using a supersensitive CGI
- Explain the difference between a CGI and a supersensitive CGI.

TOTAL VAPOR SURVEY INSTRUMENTS

TOTAL VAPOR SURVEY INSTRUMENTS

Instruments using detectors that respond to a wide variety of chemicals and give readings in the parts per million range

WHAT ARE TOTAL VAPOR SURVEY INSTRUMENTS USED FOR?

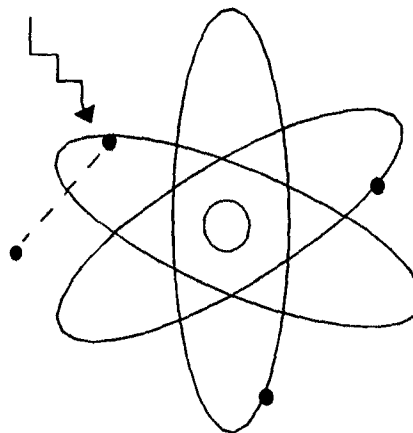
- Site characterization
- Exposure monitoring
- Soil and water sample screening
- Soil gas monitoring

NOTES

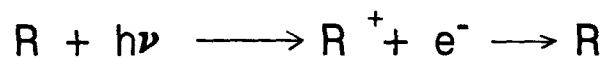
TYPES OF TOTAL VAPOR SURVEY INSTRUMENTS

- Photoionization detector (PID)
- Flame ionization detector (FID)
- Supersensitive CGI
- Metal-oxide semiconductor (MOS)

PHOTOIONIZATION



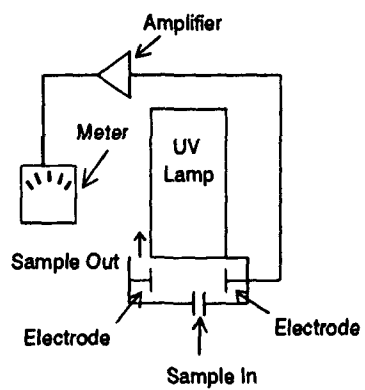
PHOTOIONIZATION



R = chemical-absorbing UV
h(nu) = photon with energy
≥ ionization potential
(IP) of chemical

NOTES

PHOTOIONIZATION DETECTOR



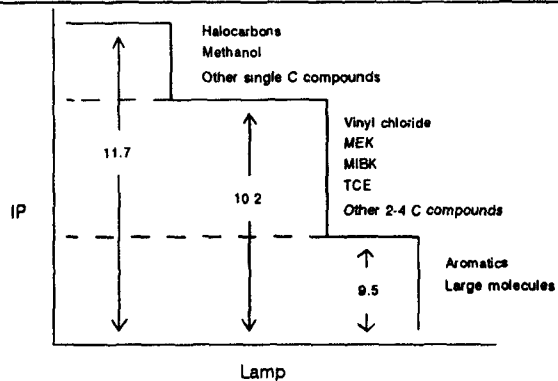
IONIZATION POTENTIAL

Chemical	IP (eV)
Carbon monoxide	14.0
Hydrogen cyanide	13.9
Methane	13.0
Hydrogen chloride	12.7
Water	12.6
Oxygen	12.1
Chlorine	11.5
Propane	11.1
Hydrogen sulfide	10.5
Hexane	10.2
Ammonia	10.1
Acetone	9.7
Trichloroethylene	9.45
Benzene	9.2
Triethylamine	7.5

NOTES

NOTES

EXAMPLES OF LAMP ENERGIES AND DETECTABLE CHEMICALS



SELECTIVE DETERMINATION OF VINYL CHLORIDE

Compound	IP
Carbon dioxide	13.8
Propane	11.1
Vinyl chloride	10.0
Acetone	9.7

PHOTOIONIZATION DETECTOR 11.7 vs. 10.2 Lamp

- 11.7 wears out faster than 10.2
- 11.7 is more susceptible to humidity
- 10.2 provides better response to chemicals it can detect

NOTES

PHOTOIONIZATION DETECTOR Considerations

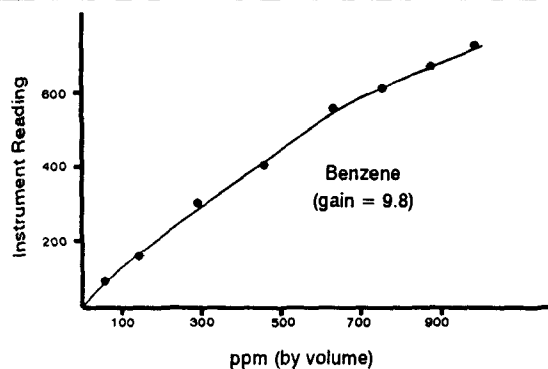
- Lamp energy/chemical IP
- Dust/humidity
- Interferences
- Electromagnetic interferences
- Lamp aging
- Relative response
- High concentrations

PHOTOIONIZATION DETECTOR Relative Response

Chemical	Relative Response*	IP
m-Xylene	1.12	8.56
Benzene	1.00	9.25
Phenol	0.78	8.69
Acetone	0.63	9.69
Isobutylene	0.55	9.25
Hexane	0.22	10.18
Ammonia	0.03	10.15

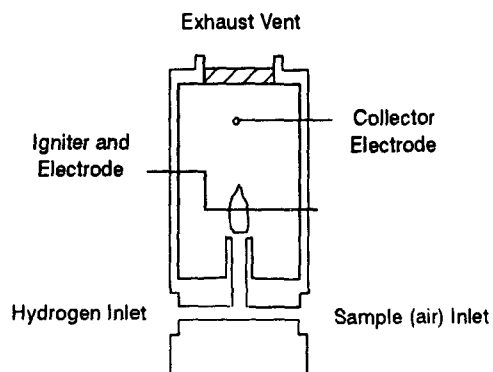
* HNU PI-101 with 10.2 eV lamp calibrated to benzene

PHOTOIONIZATION DETECTOR High Concentration Effects

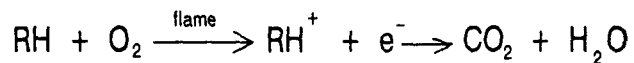


NOTES

FLAME IONIZATION DETECTOR



FLAME IONIZATION



Note: This ionization process is destructive.

COMPOUNDS GIVING LITTLE OR NO RESPONSE IN THE FID

He	N ₂	HCHO (formaldehyde)
Ar	NO	CO
O ₂	NO ₂	CO ₂
H ₂ O	N ₂ O	CS ₂
H ₂ S	NH ₃	Ethanolamine
SO ₂	HCN	

NOTES

FLAME IONIZATION Considerations

- Detects only organics
- Detects methane
- Hydrogen gas needed
- Flame out
- Electromagnetic interferences
- Relative response

FLAME IONIZATION Relative Response

Chemical	% Relative Response*
Benzene	185
Toluene	126
Methane	100
Acetone	82
Trichloroethylene	54
Freon - 12	13
Carbon tetrachloride	8

* OVA-128 calibrated to methane

SUPERSENSITIVE CGI

- Detects combustible gases and vapors
- Detector is the same as a regular CGI, but an amplifier is used to obtain ppm readings

NOTES

SUPERSENSITIVE CGI. Considerations

- Detects only combustibles
- Detects methane
- Temperature
- Chemicals that foul sensor
- Minimum oxygen
- Electromagnetic interference
- Relative response

METAL-OXIDE SEMICONDUCTOR (MOS)

- Metal-oxide coating on a ceramic substrate wrapped around a wire
- Contaminant alters conductivity by removing oxygen
- Change in current is proportional to the amount of contaminant present
- Also called "solid-state" sensor

MOS Considerations

- Saturation
- Temperature
- Minimum oxygen requirements
- Relative response

NOTES

CONCLUSION Considerations

- What the instrument can detect
- Survey, not identification
- Logistical factors
- Environmental factors
- Special features

TOTAL VAPOR SURVEY INSTRUMENTS

INTRODUCTION

Total vapor survey instruments are designed to respond to a wide range of gases and vapors. Although they lack selectivity, this broad response allows the operator to detect the presence of chemicals with one instrument. This allows the instrument to be used as a warning device during survey operations.

If the identity of a chemical is known, the instruments can be calibrated to give a one-to-one response for that chemical. If there is a mixture present, the instrument gives a total vapor reading. The detectors themselves cannot identify the components of an atmosphere. The detectors can be used in instruments, like the gas chromatograph (see *Introduction to Gas Chromatography* that are used for identification.

This section will focus on total vapor survey instruments that are used for parts per million (ppm) concentrations. It will discuss four types of toxic vapor survey instruments: photoionization detectors (PIDs), flame ionization detectors (FIDs), supersensitive combustible gas indicators (CGIs), and metal oxide semiconductors.

APPLICATIONS

Because of their ability to detect a wide range of chemicals, total vapor survey instruments are used in site survey and characterization. Although they cannot identify what chemicals are present, they can indicate what areas may have higher concentrations (hot spots) than others and delineate work areas based on levels of concentrations.

If the identities of the contaminants are known, the instruments can also be used in exposure assessment. The readings can give an approximate concentration and the information can be used in selecting exposure controls.

The instruments are also used to screen water and soil samples to determine whether further, and more complicated and expensive, analysis is needed. Usually specific reading (or any response) is used to determine which samples need further analysis.

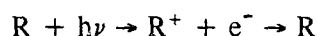
Total vapor survey instruments are also used in soil gas sampling as a screening tool to indicate "hits" and hot spots that need further sampling.

PHOTOIONIZATION DETECTORS

These instruments detect concentrations of gases and vapors in air by using an ultraviolet light source to ionize the airborne contaminant. Once the gas or vapor is ionized in the instrument, it can be detected and measured.

Principle of Operation

The photoionization process can be illustrated as:



where R is an organic or inorganic molecule and $h\nu$ represents a photon of ultraviolet (UV) light with energy equal to or greater than the ionization potential (IP) of that particular chemical species. R^+ is the ionized molecule.

When a photon of ultraviolet radiation strikes a chemical compound, it ionizes the molecule if the energy of the radiation is equal to or greater than the IP of the compound. Because ions are charged particles, they may be collected on a charged plate and produce a current. The measured current will be directly proportional to the number of ionized molecules. The R in the above equation indicates that photoionization is nondestructive and the chemical exits the detector unchanged.

PIDs use a fan or a pump to draw air into the instrument's detector. There the contaminants are exposed to UV light and the resulting negatively charged particles (ions) are collected and measured (**Figure 1**).

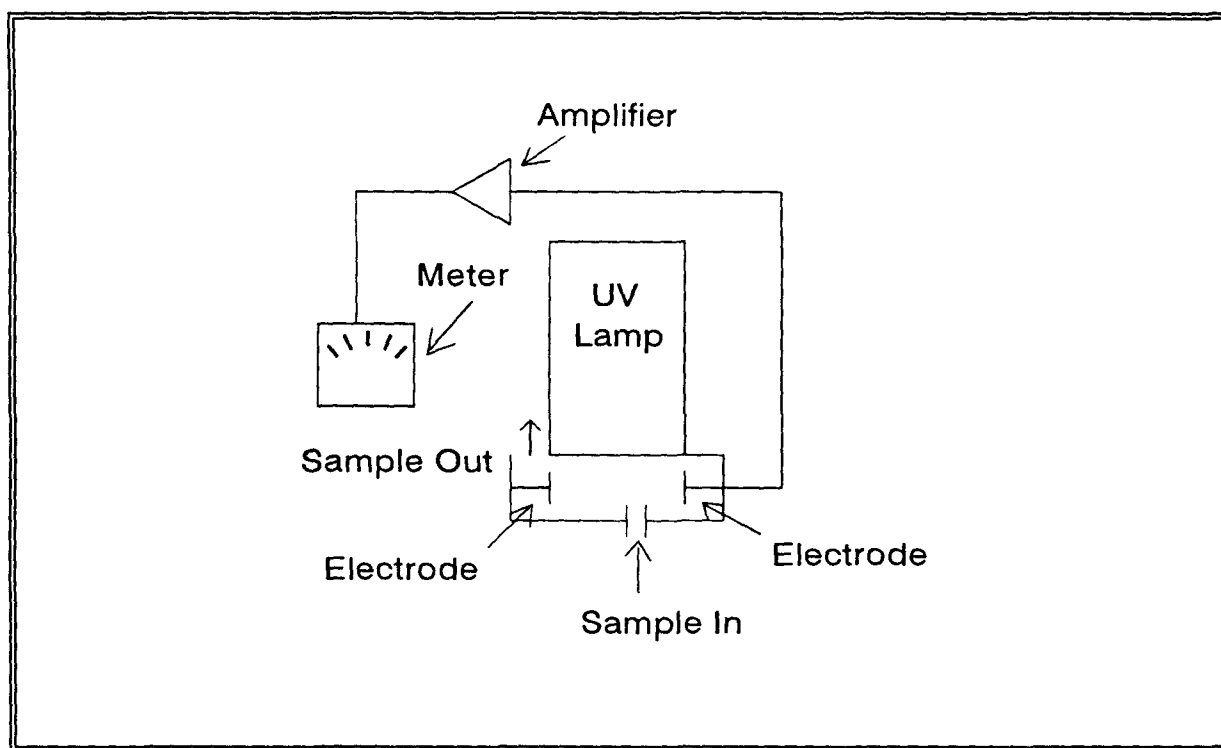


FIGURE 1. DIAGRAM OF PHOTOIONIZATION DETECTOR LAMP AND COLLECTING ELECTRODES

The energy required to remove the outermost electron from the molecule is called the ionization potential (IP) and is specific for any compound or atomic species (**Table 1**). Ionization potentials are measured in electron volts (eV).

The ultraviolet light used to ionize the chemicals is emitted by a gaseous discharge lamp. The lamps contain low-pressure gas through which a high-potential current is passed. A variety of lamps with different ionization energies are made by varying the composition of the lamp gas. The energy of lamps available are 8.4, 9.5, 10.0, 10.2, 10.6, and 11.7 eV. Not all lamps are available from a single manufacturer.

The lamp energy designation is for the predominant UV wavelength emitted by the lamp. The spectra from the lamp may have other wavelengths. Wavelengths of less energy do not have a major impact because chemicals ionized by those wavelengths will also be ionized by the predominant wavelength. The higher energy (but less photons) wavelengths will ionize the higher IP chemicals but the response will be low. Thus, a 10.2 lamp may give a response (although a small one) for a chemical with an IP of 10.9.

Photoionization Detector Considerations

Because the ability to detect a chemical depends on the ability to ionize it, the IP of a chemical to be detected must be compared to the energy generated by the UV lamp of the instrument. As discussed earlier, it may be possible to detect a chemical even if the chemical's IP is slightly greater than the lamp energy. However, the response will be poor.

TABLE 1. IONIZATION POTENTIALS OF SELECTED CHEMICALS

Chemical	Ionization Potential (eV)
Carbon monoxide	14.0
Hydrogen cyanide	13.9
Methane	13.0
Hydrogen chloride	12.7
Water	12.6
Oxygen	12.1
Chlorine	11.5
Propane	11.1
Hydrogen sulfide	10.5
Hexane	10.2
Ammonia	10.1
Acetone	9.7
Trichloroethylene	9.45
Benzene	9.2
Triethyl amine	8.0

One use for the different lamps is for selective determination of chemicals. For example, if a spill of propane and vinyl chloride were to be monitored with a PID, the first check would be to see whether the chemicals can be detected. The IP of propane is 11.1 eV and the IP of vinyl chloride is 10.0 eV. To detect both, a lamp with an energy greater than 11.1 eV is needed (like a 11.7). If vinyl chloride was the chemical of concern, then a lamp with an energy greater than 10.0 but less than 11.1 (such as 10.2 or 10.6) could be used. The propane would neither be ionized nor detected. Thus, propane would not interfere with the vinyl chloride readings.

The lamp window also affects response. The two types of windows are magnesium fluoride and lithium fluoride. The former is used for the lower energy lamps and the latter is for the 11.7 eV lamp. The lithium fluoride is used to permit the higher energy photons to be emitted. Lithium fluoride has two disadvantages. The first is that humidity and the high-energy photons degrade the window. This reduces the life span of the lamp. The 11.7 eV lamps are expected to have a life expectancy one-tenth of that of 10.2 or 10.6 lamps. The second disadvantage is that lithium fluoride also limits the amount of photons being emitted. Thus, if both a 10.2 and an 11.7 lamp have enough energy to ionize a chemical (e.g., a chemical with an IP of 9.7), the 10.2 may give a higher response because it is emitting more light.

The sample drawn into the instrument passes over the lamp to be ionized. Dust in the atmosphere can collect on the lamp and block the transmission of UV light. This will cause a reduction in instrument reading. The lamp should be cleaned regularly. Newer models of PIDs have dust filters.

Humidity can cause two problems. When a cold instrument is taken into a warm moist atmosphere, the moisture can condense on the lamp. Like dust, this will reduce the available light. Moisture in the air can also reduce the readings. It is thought that the water molecules collide with the ionized chemical and deactivate them. This reduction in response has been reported to be as much as 50% for a relative humidity of 90%. As mentioned earlier, the 11.7 lamp window is especially sensitive to moisture.

Because an electric field is generated in the sample chamber of the instrument, radio-frequency interference from pulsed DC or AC power lines, transformers, generators, and radio wave transmission may produce an error in response.

As the lamp ages, the intensity of the light decreases. It will still have the same ionization energy, but the response will decline. This will be detected during calibration and adjustments can be made. However, the lamp will eventually burn out.

Methane can act as an interference by absorbing the UV energy without ionization. This reduces the ionization of other chemicals present. The net effect is a reading lower than the true concentration.

Although oxygen is not needed for photoionization, a change in oxygen will affect the response. Thus, there are oxygen limits for their use. The instruments are calibrated and used in normal oxygen atmospheres. The HNU PI-101 requires a minimum of 10% oxygen for reliable results.

Photoionization detectors are calibrated to a single chemical. The instrument's response to chemicals other than the calibration gas/vapor can vary. **Table 2** shows the relative responses of several chemicals for a specific PID.

In some cases, at high concentrations the instrument response can decrease. While the response may be linear (i.e., 1 to 1 response) from 1 to 400 ppm for an instrument, a concentration of 900 ppm may only give a meter response of 700 (**Figure 2**). Some instruments use a microprocessor to compensate for this effect by storing calibration information for the high concentrations.

Manufacturers who make photoionization detectors can be found in this manual in the *Manufacturers and Suppliers of Air Monitoring Equipment* section.

**TABLE 2. RELATIVE RESPONSES FOR SELECTED
CHEMICALS USING THE HNU MODEL PI 101
WITH 10.2 eV PROBE CALIBRATED TO BENZENE**

Chemical	Relative Response
m-Xylene	1.12
Benzene	1.00
Acetone	0.63
Isobutylene	0.55
Vinyl chloride	0.50
Hexane	0.22
Phosphine	0.20
Ammonia	0.03

Source: *Instruction Manual for Model PI 101, Portable Photoionization Analyzer*, HNU Systems, Inc., Newton, MA, 1986.

Examples of Photoionization Detector Instruments

HNU Systems, Inc.

HNU Systems, Inc., manufactures four models of photoionization detector survey instruments: PI-101, IS-101, HW-101, and the DL-101.

All four consist of two modules connected via a single power cord (**Figure 3**):

- A readout unit having an analog meter or digital display, a rechargeable battery, and power supplies for operation of the amplifier and the UV lamp
- A sensor unit consisting of the UV light source, pump, ionization chamber, and a preamplifier.

The **PI-101** has a fan instead of a pump and cannot draw a sample through a resistance (like a piece of long tubing). The PI-101 is rated for Class I, Division 2, Group A, B, C, and D locations.

The **IS-101** is similar to the PI-101 except it is intrinsically safe for Division 1 locations.

The **HW-101** has a pump instead of a fan, so it can be used to draw a sample through tubing or through a probe used for soil gas sampling. The HW-101 also has a dust filter and is more moisture resistant than the other models. It also has a light-emitting diode (LED) display on the handle that indicates concentration changes.

The **DL-101** has a pump and dust filter like the HW-101. However, it has many different fixtures than other units. It has a pistol grip for holding the probe. There is a LED display on the handle. The instrument has a datalogger to store calibration information and to record time and location of readings. Information from the datalogger can be transferred to a computer. It has a digital readout instead of an analog meter.

These units have a separate sensor unit because the lamps available - 9.5, 10.2 (standard), and 11.7 eV - require separate electronic circuits. To change the energy of ionization, the whole sensor or

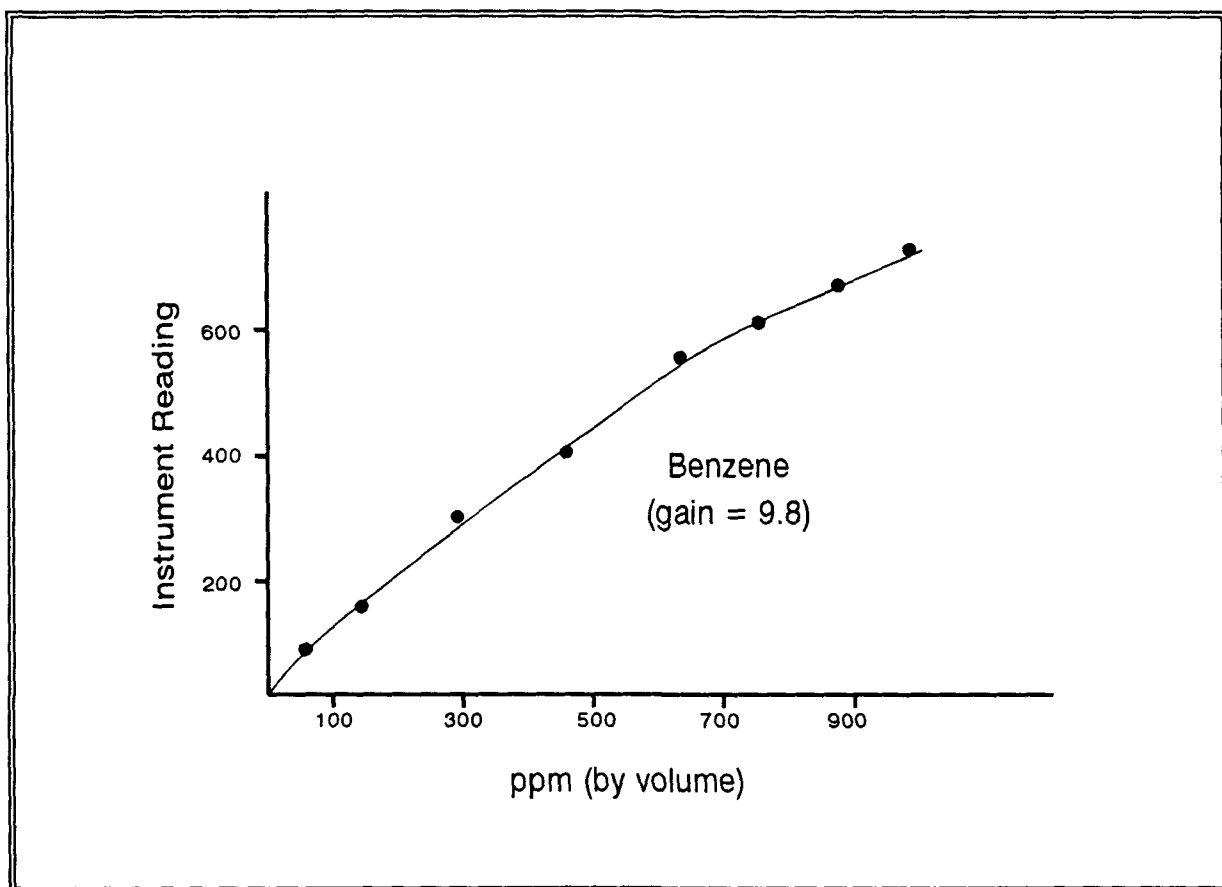


FIGURE 2. TYPICAL CALIBRATION CURVE FOR PHOTOIONIZATION ANALYZER

Source: *Instruction Manual for Model PI-101 Photoionization Detector*, copyright 1975, HNU Systems, Inc.; reprinted with permission of publisher.

probe has to be switched, not just the lamp. The exception is the DL-101. With the DL-101, lamps can be interchanged and the datalogger/microprocessor makes the proper adjustments. In all models the lamps are replaceable.

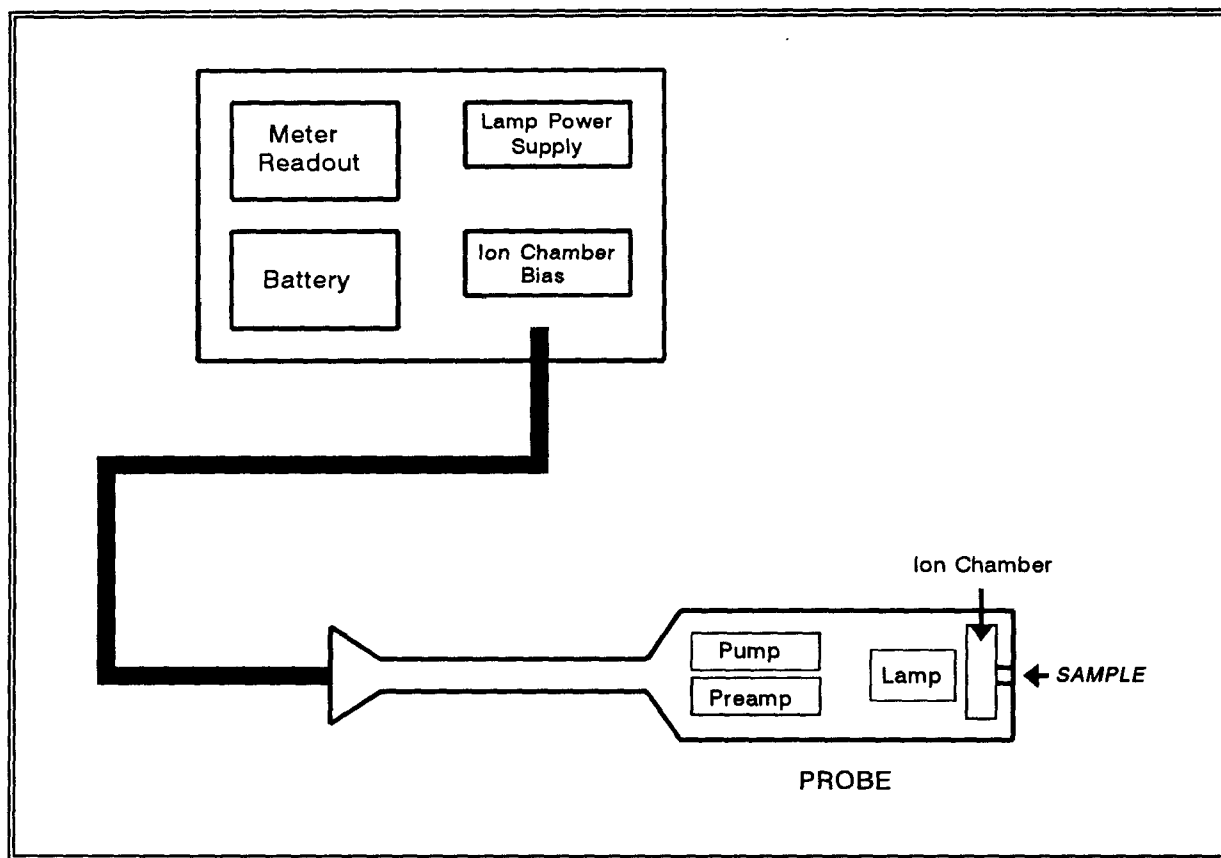


FIGURE 3. PORTABLE PHOTOIONIZATION DETECTOR

Source: *Instruction Manual for Model PI-101 Photoionization Detector*, copyright 1975, HNU Systems, Inc.; reprinted with permission of publisher.

Photovac, Inc.

Photovac has three versions of its **MicroTIP®**. All three have a microprocessor that is used to calibrate the instrument and a datalogger to store data. Information from the datalogger can be transferred to a computer. The standard lamp is 10.6 eV, but it can be easily replaced with a 8.4, 9.5, 10.2 or 11.7 eV lamp. The readout is digital with a range of 0 to 2000. They all have a dust filter. The **MP-1000** does not have a inherent safety approval. The **HL-2000** is approved for Class I, Division 2, Groups A, B, C, and D locations. The **IS-3000** is intrinsically safe.

Thermo Environmental Instruments

The **Organic Vapor Meter (OVM) Model 580B** is 5" by 5" by 10" with a handle in the center on top. It can use any of four different lamps - 9.6, 10.0, 10.6 and 11.8 eV. The instrument has a digital readout with a range of 0 to 2000. It has a maximum hold feature so that you can get two readings - the current concentration or the maximum concentration during the survey. The meter has a lock-out if the readout exceeds 2000 so that high concentrations are not missed. It must be reset in an area of low concentrations. The instrument has a microprocessor for assistance in calibration and lamp changing.

The **OVM-580S** is similar to the 580B, but is intrinsically safe.

Both have connections and software for interfacing the unit with a personal computer. They also have a datalogger for recording readings at coded locations so that the readings can be looked at later or downloaded into a computer.

Photoionization detectors are also used in gas chromatographs made by Photovac, HNU and Thermo Environmental Instruments. Gas chromatography will be discussed in a later section.

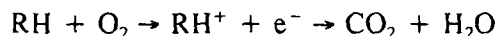
FLAME IONIZATION DETECTOR

These units use a flame to ionize airborne contaminants. Once they are ionized, they can be detected and measured.

Principle of Operation

FIDs use a hydrogen flame as the means to ionize organic vapors. FIDs respond to virtually all organic compounds; that is, compounds that contain carbon-hydrogen or carbon-carbon bonds. FIDs will not respond to inorganic compounds.

Inside the detector chamber, the sample is exposed to a hydrogen flame which ionizes the organic vapors (**Figure 4**):



When most organic vapors burn, positively charged carbon-containing ions are produced. These can be collected by a negatively charged collecting electrode in the detector chamber. An electric field exists between the conductors surrounding the flame and a collecting electrode. As the positive ions are collected, a current proportional to the hydrocarbon concentration is generated on the input electrode. This current is measured with a preamplifier which has an output signal proportional to the ionization current. A signal conducting amplifier is used to amplify the signal from the detector and to condition it for subsequent meter or external recorder display.

Flame ionization detectors have a more generalized response in detecting organic vapors. This generalized sensitivity is due to the breaking of chemical bonds which require a set amount of energy and is a known reproducible event. When this is compared to photoionization (PID), a major

difference should be noted between the detectors. PID detection is dependent upon the ionization potential (in eV) and the ease in which an electron can be ionized (displaced) from a molecule. This mechanism is variable, highly dependent on the individual characteristics of a particular substance. This results in a more variable response factor for the vast majority of organics that are ionizable. Therefore, in general, one does not see large sensitivity shifts between different substances when using an FID as compared to a PID. FIDs are the most sensitive for saturated hydrocarbons (alkanes), unsaturated hydrocarbons (alkenes and alkynes), and aromatic hydrocarbons. Substances that contain substituted functional groups, such as hydroxide (OH) and chloride (Cl), tend to reduce the detector's sensitivity.

Companies that manufacture FIDs are listed in the *Manufacturers and Suppliers of Air Monitoring Equipment* section. The Foxboro Century Organic Vapor Analyzer (OVA) will be discussed as an example later.

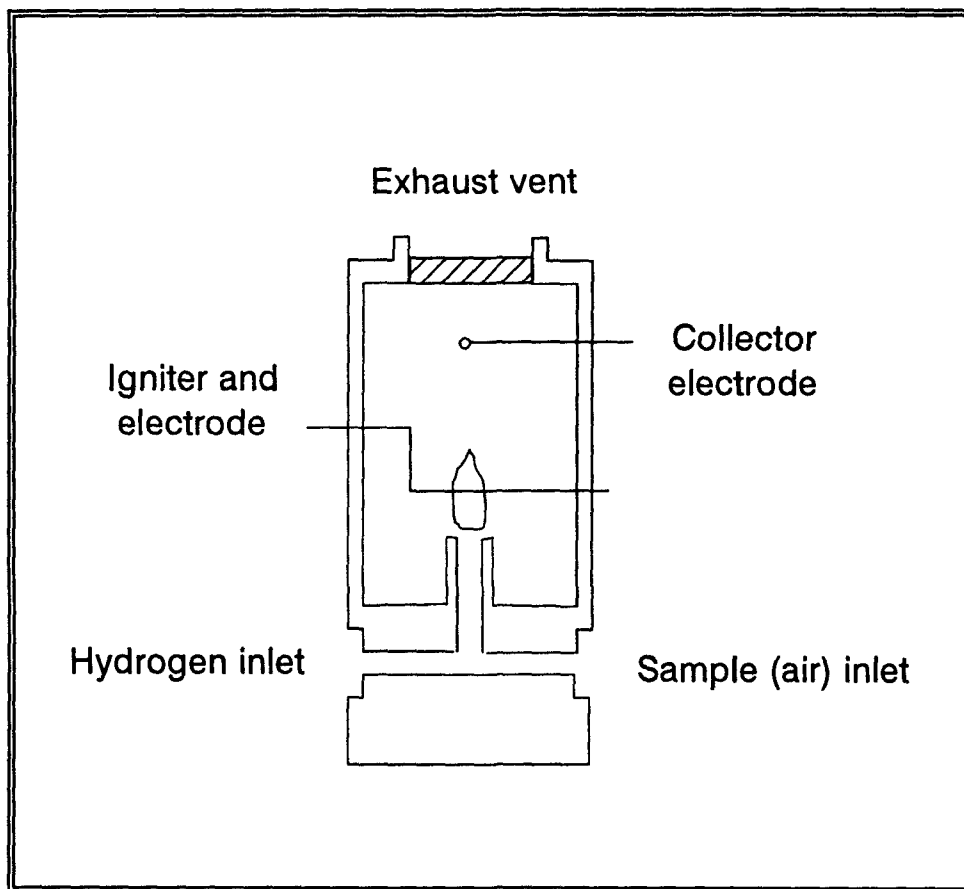


FIGURE 4. EXAMPLE OF A FLAME IONIZATION DETECTOR SCHEMATIC

Flame Ionization Detector Considerations

Flame ionization detectors respond only to organic compounds. Thus, they do not detect inorganic compounds like chlorine, hydrogen cyanide, or ammonia. There are some carbon containing chemicals for which the FID gives little or no response also. **Table 3** illustrates this situation.

**TABLE 3. CHEMICALS GIVING LITTLE OR NO RESPONSE
WITH FLAME IONIZATION DETECTORS**

He	N ₂	HCHO (formaldehyde)
Ar	NO	CO
O ₂	NO ₂	CO ₂
H ₂ O	N ₂ O	CS ₂
H ₂ S	NH ₃	TDI
SO ₂	HCN	ethanol amine

Source: *Relative Response Data Sheet for Organic Vapor Analyzer*,
January 16, 1989. The Foxboro Company.

Flame ionization, unlike photoionization, is a destructive form of monitoring. Typically, the combustion products are carbon monoxide and water. However, substituted hydrocarbons (e.g. chlorinated compounds) may produce toxic or corrosive byproducts.

The FID responds very well to methane. Methane is used as a calibration gas for many FIDs. However, if monitoring is being done near a landfill or in a sewer system, the methane can mask the response to low concentrations of other organics.

Hydrogen gas is used as fuel for the flame. This requires the extra logistics of maintaining a hydrogen gas supply and recharging the instrument. It also involves working with a flammable compressed gas.

Inadequate oxygen can cause the flame to go out. High concentrations of organics can also cause a flame out. Without the flame, there is no detection.

Cold weather can also cause the flame to extinguish or inhibit startup (ignition) of the instrument.

Because an amplifier is used to enhance the signal from the detector, radio-frequency interference from pulsed DC or AC power lines, transformers, generators, and radio wave transmission may produce an error in response.

As with all instruments, flame ionization detectors respond differently to different compounds. **Table 4** is a list of the relative responses of the Foxboro CENTURY OVA to some common organic compounds. Since that instrument is factory calibrated to methane, all responses are relative to methane and are given by percentage, with methane at 100%.

**TABLE 4. RELATIVE RESPONSES FOR SELECTED
CHEMICALS USING THE OVA CALIBRATED TO METHANE**

Compound	Relative Response (%)
Methane	100
Ethane	77
Propane	70
Acetylene	225
Benzene	185
Toluene	126
Acetone	82
Methanol	12
Isopropyl alcohol	65
Carbon tetrachloride	8
Freon-12	13
Trichloroethylene	54

Source: Product Literature, The Foxboro Company; used
with permission of The Foxboro Company.

Examples of Flame Ionization Detector Instruments

Foxboro CENTURY Organic Vapor Analyzer (OVA)

One of the more common FID instruments is the Foxboro CENTURY OVA. There are two models: the OVA-128 and the OVA-108. Both consist of two major parts (**Figure 5**):

- A 12-pound package containing the sampling pump, battery pack, support electronics, flame ionization detector, hydrogen gas cylinder, and an optional gas chromatography (GC) column.
- A hand-held meter/sampling probe assembly.

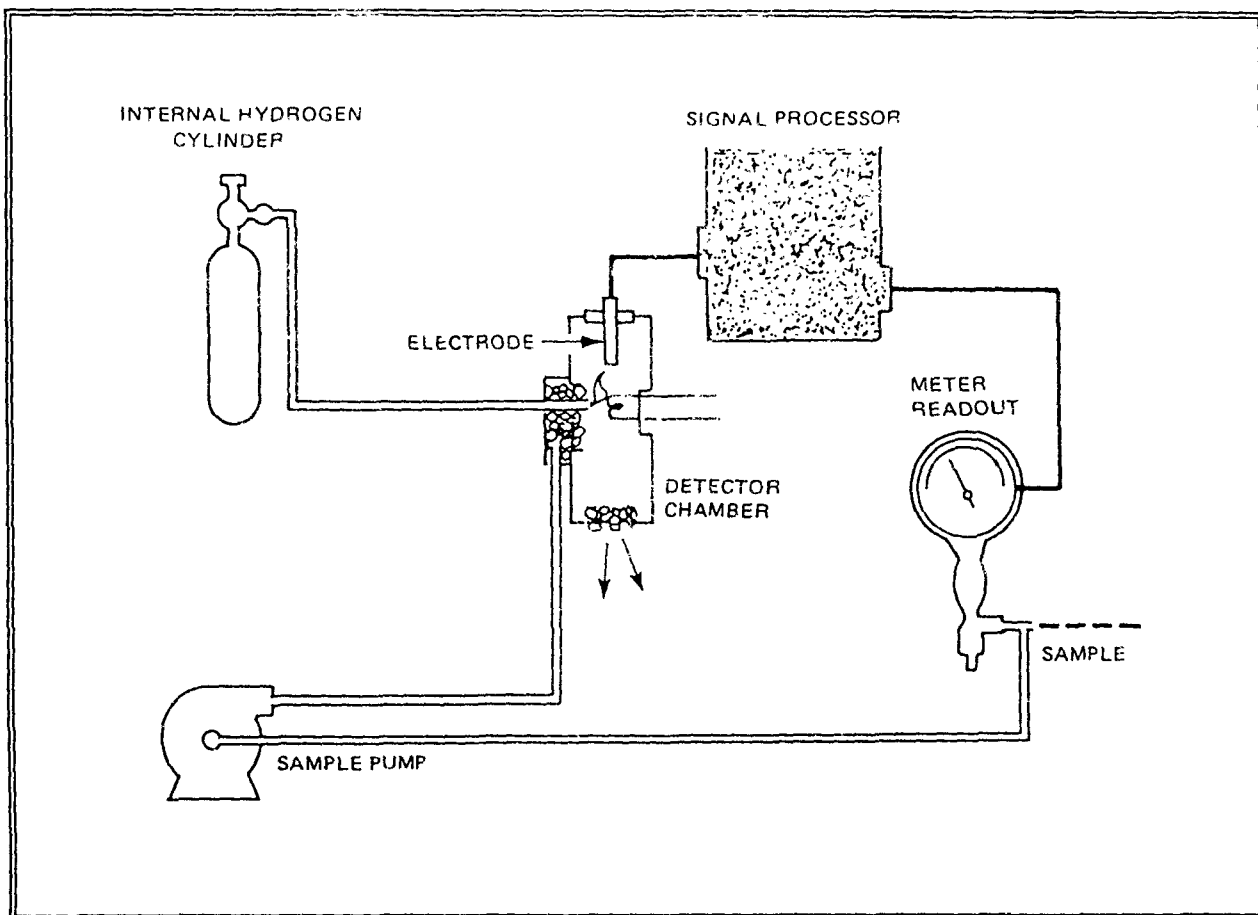


FIGURE 5. ORGANIC VAPOR ANALYZER SCHEMATIC

Source: Product Literature, The Foxboro Company; used with permission of The Foxboro Company.

The OVA-128 has a range of 0-1000 ppm. The OVA-108 reads from 0-10,000. Both are intrinsically safe for Class 1, Division 1, Groups A, B, C and D. Both models are factory calibrated to methane, but can be calibrated to other chemicals.

Other FID units are the Sensidyne **Portable FID**, Heath Consultants **Porta-FID II**, and Summit Industries **SIP-1000**. The Portable FID and the SIP-1000 have gas chromatograph options.

Combination PID and FID

Foxboro also manufactures the TVA-1000. The instrument can use a PID, an FID, or both. The instrument has datalogging capabilities and digital readouts on a probe and side pack.

SUPERSENSITIVE COMBUSTIBLE GAS INDICATORS

The CGI is a type of total vapor survey monitor. However, the normal range for a CGI is in the percent LEL concentration. This range is too high for toxic concentration monitoring. Super-sensitive combustible gas indicators use the combustible gas sensor with circuitry to amplify the signal. Instead of measuring per cent of the LEL, the readout is in part per million. Because the detection is based on combustion, the instruments can detect both organic and inorganic combustible gases/vapors.

Some units—like the Bacharach TLV Sniffer—only measure in the ppm range. Other units (e.g., the GasTech Model 1314) can be switched from percent LEL to ppm readout.

These units have the same limitations and considerations as the regular combustible gas indicators. In some cases, like sensitivity to temperature changes, the effects are a bigger problem because of the amplifier circuit. Because of the amplifier, they are more sensitive to electromagnetic radiation than standard combustible gas indicators.

METAL-OXIDE SEMICONDUCTORS (MOS)

MOS, also called solid-state sensors, consist of a metal oxide film coating on a heated ceramic substrate fused or wrapped around a platinum wire coil. When a gas comes in contact with the metal oxide, it replaces oxygen in the oxide and alters the conductivity of the semiconductor. The change in conductivity can be expressed in a meter readout. The bead is heated to give a constant baseline as oxygen in the air can combine with the oxide. Oxygen can combine with the sensor to cause an instrument response.

Selectivity can be determined by selecting specific metal oxides and/or using specific temperatures from the heater to prevent chemicals reacting. To use as a toxic atmosphere survey monitor, the sensor should respond to a wide variety of chemicals. Thus, the sensor should be designed to be nonselective.

Examples of instruments using a MOS for a total vapor sensor are the **AIM 2000/3000** and the **Dynamation Model CGM™**.

CONCLUSION

This section has described several types of detectors used for monitoring the presence of a wide range of gases and vapors. While these are not the only types of detectors or monitors available, they are the more commonly used devices for field surveys.

AIR SAMPLE COLLECTION

PERFORMANCE OBJECTIVES

At the end of this lesson, participants will be able to:

- List four advantages to using air sample collection
- List three sources of sampling and analysis methods
- List three considerations when using liquid sorbent samplers
- List three considerations when using solid sorbent samplers
- List three considerations when using whole air samplers
- Describe two methods of collecting whole air samplers.

AIR SAMPLE COLLECTION

DIRECT-READING INSTRUMENTS (DRI) vs. AIR SAMPLE COLLECTION

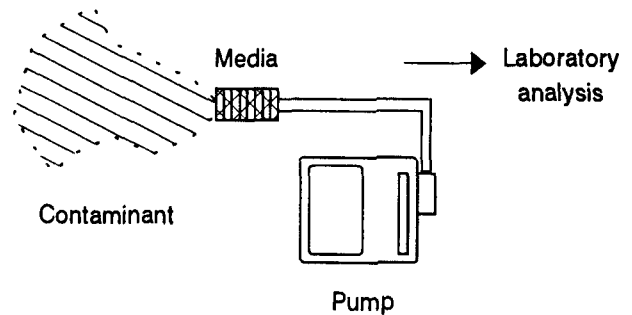
<u>Features</u>	<u>DRI</u>	<u>Air Sample Collection</u>
Response time	Seconds to minutes	Hours to days
Quantitative	Yes	Yes
Identification	No	Yes
Detection range	Parts per million (ppm) to percent	Parts per trillion (ppt) to parts per million (ppm)
Cost	Inexpensive	Expensive

AIR SAMPLE COLLECTION Uses

- Identify and quantify airborne chemicals onsite
- Evaluate personal exposures
- Evaluate releases from site
- Data for public health/ecological risk assessment

NOTES

AIR SAMPLE COLLECTION Components



COLLECTION AND ANALYTICAL METHODS

- EPA
 - *Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air*
 - *Compendium of Methods for Determination of Air Pollutants in Indoor Air*
 - *Compendium of Methods for Determination of Toxic Inorganic Compounds in Ambient Air*

COLLECTION AND ANALYTICAL METHODS

- *NIOSH Manual of Analytical Methods*
- *OSHA Analytical Methods Manual*
- American Society for Testing and Materials
- Specialty methods

NOTES

COLLECTION AND ANALYTICAL METHODS

- Air Methods Database
 - Combines previous methods into a database
 - Free from EPA
 - See fact sheet

COLLECTION MEDIA Types of Contaminants

- Aerosols/particulates (nonvolatile)
- Gases and vapors (volatile)
- Combination (semivolatile)

FILTER MEDIA Examples

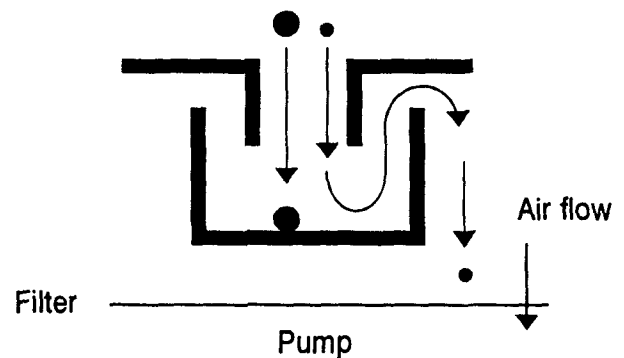
<u>Filter Media</u>	<u>Application</u>
0.8-micron (μ) mixed cellulose ester (MCE)	Metals; asbestos
Glass fiber	Pesticides
Polyvinyl chloride (PVC)	Total particulates; hexavalent chromium
Polytetrafluoroethylene	Alkaline dusts

NOTES

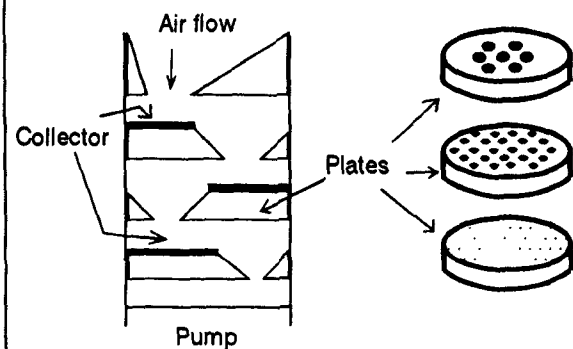
AEROSOLS/PARTICULATES Size Selection Terminology

- Total suspended particulate (TSP)
- Particulate matter - 10μ (PM-10)
- Total
- Respirable

AEROSOL SIZE SELECTION Inertial Impactor



AEROSOL SIZE SELECTION Cascade Impactor



NOTES

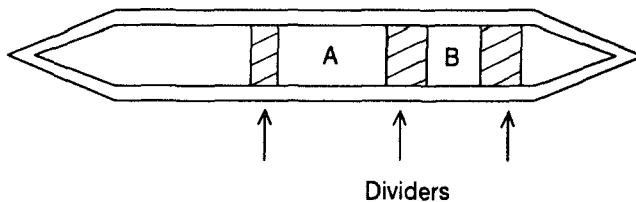
GASES AND VAPORS Examples

- Organic vapors
 - Benzene
 - Trichloroethylene
 - Ethyl alcohol
- Inorganic gases
 - Ammonia
 - Hydrogen cyanide
 - Hydrogen chloride

SOLID SORBENT MEDIA Examples

<u>Solid Sorbent</u>	<u>Compound</u>
Activated carbon	Nonpolar organics (NIOSH)
Tenax [®]	Volatile, nonpolar organics (EPA)
Carbon molecular sieve	Highly volatile, nonpolar organics (EPA)
Silica gel	Polar organics (NIOSH)

SOLID SORBENT TUBE Example



A = Solid sorbent
B = Solid sorbent (backup or different sorbent)

NOTES

SOLID SORBENT CONSIDERATIONS

- Breakthrough
- Sorption efficiency
- No universal media
- Stability/handling
- Desorption
 - Thermal
 - Solvent

LIQUID SORBENT MEDIA Examples

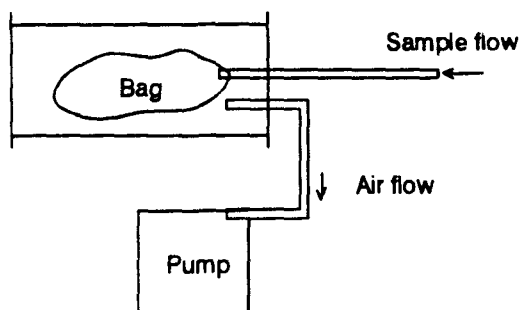
<u>Media</u>	<u>Compound</u>
0.1N NaOH	Cresol/phenol (EPA) Phenol (NIOSH)
Aniline	Phosgene (EPA)
DNPH reagent + isooctane	Aldehydes/ketones (EPA)
0.1M HCl	Hydrazine (NIOSH)

LIQUID SORBENT CONSIDERATIONS

- Spillage
- Fragile holders
- Hazardous liquids?
- Stability
- Evaporation

NOTES

WHOLE AIR COLLECTION "Sampling Lung"



Source: "Sampling and Analysis of Emissions from Stationary Sources," Schuetzle et al., *Journal of the Air Pollution Control Association*, Volume 25, No. 9, Sept 1975.

BAG SAMPLING vs. CANISTER SAMPLING

<u>Bag</u>	<u>Canister</u>
Grab	Integrated
Need field pump	Need lab pump
Less stable sample	More stable sample
Cannot clean	Clean to reuse
Disposable	Reusable
Cannot pressurize	Can pressurize

COMBINATION MEDIA Examples

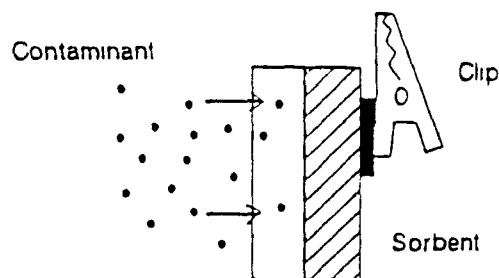
<u>Media</u>	<u>Compound</u>
Quartz filter + polyurethane foam (PUF)	PCBs/pesticides (EPA) PAHs (EPA)
Quartz filter + XAD-2	PAHs (EPA)
Glass filter + Florisil®	PCBs (NIOSH)
MCE filter + 0.1N KOH	Cyanides (NIOSH)

NOTES

SAMPLING PUMPS

- Most collection methods require a pump to pull air through medium
- Exceptions
 - Evacuated canister
 - Passive dosimeter

PASSIVE DOSIMETER Example



Chemical permeates membrane and/or diffuses into sampler

PASSIVE DOSIMETERS Considerations

- No pump
- Sorbent limits
 - Breakthrough
 - Humidity
 - Temperature
- Early and late exposure problems
- Gases and vapors only

NOTES

SAMPLE PUMPS High Flow Rates

- Greater than 10 cubic feet per minute
- Ambient air sampling

SAMPLE PUMPS Medium/High Flow Rates

- 1 to 6 liters per minute
- Personal sampling
- Aerosol sampling

SAMPLE PUMPS Low Flow Rates

- 10 to 750 cubic centimeters (milliliters) per minute
- Personal sampling
- Gas and vapor sampling

NOTES

SUMMARY

- Collect sample for laboratory analysis
- Determine whether air sampling is appropriate
- Identify appropriate air sampling method

AIR SAMPLE COLLECTION

INTRODUCTION

The types of equipment discussed in this section are media (filters and sorbents), containers (gas bags and canisters) and pumps for collecting air samples. Unlike direct-reading instruments that give immediate results, these samples must be analyzed by instruments that are not usually taken onsite. The analysis may be done in the support area of a site or at a laboratory many miles away. This causes a delay in receiving information. However, there are advantages to their use.

- The chemicals in the atmosphere can be concentrated so that the detection limit can be lower than for a direct-reading instrument, even when the same type of detector is used.
- Specialized detectors can be used. Some detectors (e.g., PID and FID) are used in both direct-reading instruments and analytical instruments. However, some detectors are only found in analytical instruments (e.g., electron capture detector). For specific analysis of aerosols (e.g., lead), there are no direct-reading instruments. A sample must be collected and then analyzed by a nonportable instrument.
- The analytical instruments used generally allow identification and quantification of the chemicals. Instead of a total vapor reading, it may be possible to get an identification and concentration of the components.
- The collection devices allow long duration (hours to days) and unattended sampling.

SAMPLE COLLECTION COMPONENTS

General

The basic components of a sample collection system are:

- A collection media for separating the contaminants from the atmosphere or a collection container for holding part of the atmosphere.
- A pump to pull air through the media to push the sample into a container. When a pump is used, the method is called "active" sampling. Some methods do not require a pump and are called "passive" samplers.
- A method to analyze the collected sample. This part will not cover the analysis of a sample. A limited discussion of analyses and detector types is found in *Total Vapor Survey Instruments* and *Introduction to Gas Chromatography*.

Selection of Components

Several factors affect the selection of the components for a sample collection system. These include 1) the chemical and physical properties of the chemical to be collected, 2) the purpose of the sample, 3) the analytical method used by the laboratory, 4) the laboratory's capability to do a specific procedure and their experience with the method, and 5) equipment characteristics. The following elaborate on these factors:

- Chemical and physical properties of the chemical—The chemical/physical properties of the chemical to be collected affect the type of media used. Volatile chemicals pass readily through a filter. Therefore, some kind of sorbent is needed. In some cases, a reaction, like an acid gas with an alkaline solution, may be used instead of sorption.
- Purpose of the sample—Two types of samples are the "personal" sample and the "area" sample:
 - Personal sample—A personal sample requires a pump that can be worn by the person being sampled. This means the pump must be compact and battery operated. A personal sample is used to evaluate the exposure level of the person being sampled. The sample results are usually compared to an exposure limit (see *Exposure Limits and Action Levels*). A personal sample collects the contaminants in the "breathing zone," a 12-inch-radius hemisphere in front of the wearer's nose.
 - Area sample—An area sample, to determine chemicals and concentrations in a specific area, can use the same type of pump. However, area samples generally are for checking lower concentrations than personal samples. This is because they are used for identification or evaluation of public exposure. The lower concentrations require a larger volume of air to concentrate the sample. This can be done by using a higher flow rate, by sampling longer, or both. Longer sampling times are used because public exposure can be 24 hours each day compared to a site worker's exposure of 8 to 10 hours each day. A long sampling time and a high flow rate require a pump that is AC powered. Battery pumps are only rated for 8 to 10 hours of use.
- Analytical method used by the laboratory—The analytical method used by the laboratory also affects the collection devices used. There are commonly used methods developed by the U.S. Environmental Protection Agency (EPA), National Institute of Occupational Safety and Health (NIOSH), and Occupational Safety and Health Administration (OSHA) that specify sampling and analysis procedures. These methods are found in EPA's *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, NIOSH's *Manual of Analytical Methods*, and OSHA's *Analytical Methods Manual*.

Although these methods were developed for similar chemicals, there are differences in the procedures. The laboratory being used may also have different requirements. The laboratory should be consulted prior to sampling.

EPA's Environmental Response Team (EPA-ERT) has developed an *Air Methods Database* so that the user can determine what methods are available for sampling a chemical. The database includes EPA, NIOSH, OSHA, and American Society for Testing and Materials (ASTM) methods. Further information is found in a technical bulletin (Appendix A).

- Capability of the laboratory—When you choose a laboratory for analysis, make sure you consider its capability to do a specific procedure and its experience with the desired method. For NIOSH and OSHA methods, use an American Industrial Hygiene Association (AIHA) accredited laboratory.
- Equipment characteristics—This is an important consideration. For example, some pumps have timers that may be useful or even necessary. Some collection devices are fragile and may not be desirable under certain operating conditions.

AEROSOL (NONVOLATILE CHEMICALS) SAMPLERS

Media

Airborne aerosols include both dispersed liquids (mists and fogs) and solids (dusts, fumes, and smoke). The most common method of sampling aerosols, especially the solids or particulates, is to trap them on filters using active systems. Impingers (see *Liquid Sorbents* in the *Gas and Vapor (Volatiles) Samplers* section) have been used, but filters are more convenient. Two types of filters are used.

- Fiber filters are composed of irregular meshes of fibers forming openings or pores of 20 μm in diameter or less. As particulate-laden air is drawn through such filters, it is forced to change direction. Particulates then impinge against the filter fibers and are retained. A number of fiber filters are available (**Table 1**). The two with the greatest application to hazardous materials operations are cellulose and glass. Filters of these materials typically consist of thick masses of fine fibers and have low mass-to-surface area ratios. Of the two, cellulose is the least expensive, is relatively low in ash, has high tensile strength, and is available in a variety of sizes. Its greatest disadvantage is its tendency to absorb water, thus creating problems in weighing.
- Membrane filters are microporous plastic films formed by precipitating a resin. Pore sizes of 0.01–10 μm can be formed during manufacture. Membrane filters act as a sieve with collection of most particulates on the surface. This can be useful for visual examination of the sample. This group of filters includes such materials as cellulose ester, polyvinyl chloride, and polytetrafluoroethylene (**Table 1**). These filters have an extremely low mass and ash content. Some are completely soluble in

organic solvents. This allows particulates to be concentrated into a smaller volume for analysis.

TABLE 1. FILTER MEDIA FOR AIRBORNE PARTICULATES

Filter Medium	Representative Application/Analysis
Mixed cellulose ester (MCE), 0.8- μ m pore	Metals/atomic adsorption; asbestos/phase contrast microscopy
Glass fiber	Pesticides/various
Polyvinyl chloride (PVC)	Total particulates/gravimetric; hexavalent chromium/visible spectrophotometry
Polycarbonate	Fibers
Polytetrafluoroethylene	Alkaline dusts/acid-base titration

Source: NIOSH *Manual of Analytical Methods*, Third Edition, Volume 1, February 1984 and supplements.

Filter sizes range from 13 mm in diameter to 40 by 40 inches. Small sizes (25 mm and 37 mm diameter) are generally used for personal samples and the larger sizes are normally used for Hi-Vol sampling. Selection of the size and type of filter depends on the user application and analysis. **Table 1** gives examples of different filters and their applications.

The common filter holder used for personal samples is the polystyrene plastic cassette (**Figure 1**). It consists of two or three stacked sections, the number depending on the contaminant and the collection method. The sections of a cassette are molded to fit tightly when stacked and to tightly grip the outer edge of the filter. Each cassette has end plugs to seal the inlet and tubing connector part once the sample collection is completed.

Other materials than polystyrene can be used. Metal is used in large samplers with high flow rates. Carbon-filled polypropylene is used for asbestos sampling because it prevents an accumulation of a static charge, which would result in the attraction of the asbestos fibers to the cassette walls.

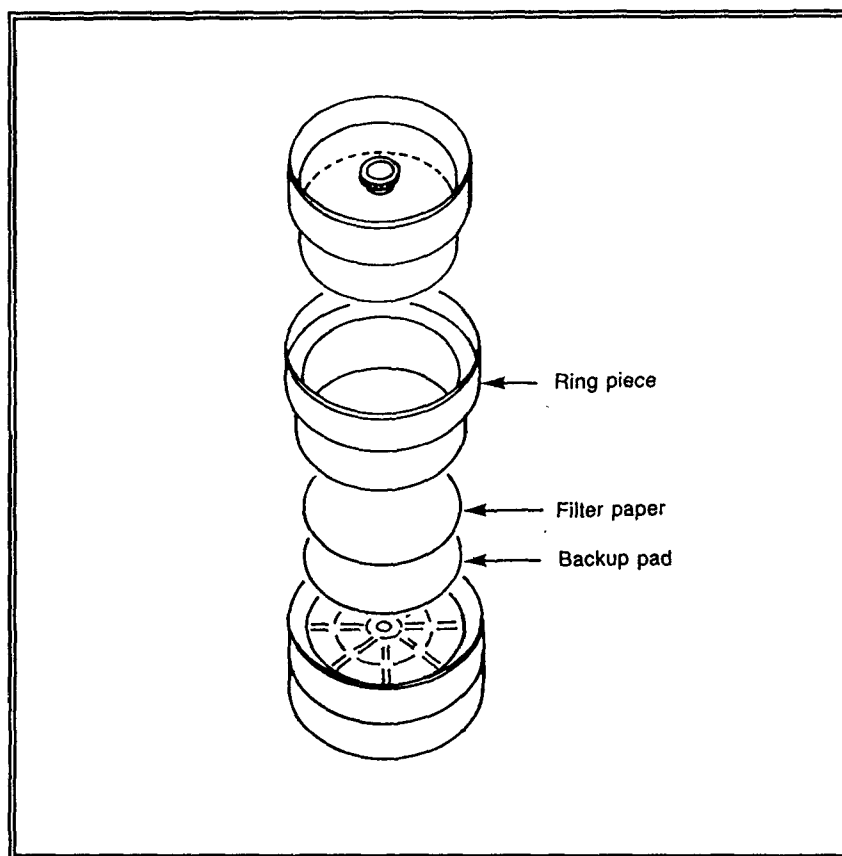


FIGURE 1. ASSEMBLY OF A THREE-PIECE FILTER CASSETTE

Source: *OSHA Technical Manual*, U.S. Department of Labor, OSHA, 1990.

Size Selection

Unlike gases and vapors, not all aerosols reach the deeper portions of the respiratory system. The nose and bronchioles remove the larger sizes. Environmental or public health samples are usually classified as total suspended particulates (TSP) or particulate matter - 10 μ (PM_{10}). PM_{10} samples collect particulates that are 10 μ and smaller. This represents the fraction of airborne particles that would be inhaled. PM_{10} samples are used to assess the inhalation route of exposure. TSP is used to assess exposure to contaminants that may be deposited downwind and available through ingestion.

Occupational samples are classified as total or respirable. Total samples are equivalent to TSP. Respirable samplers are designed to collect particles that would reach farther into the respiratory system. Most occupational exposure limits for particles are based on total samples. A few, silicon dust, coal dust, and nuisance dust, are based on respirable samples.

The most common devices used for aerosol size separation are the inertial impactor, the centrifugal separator, and the cascade impactor.

- The inertial impactors rely on a sudden change in velocity and direction to separate the sizes of particles. **Figure 2** illustrates the principle. The example shows that the larger particles (having more inertia) cannot follow the change in air direction and impact in the separator. The smaller particles can make the turns and are collected at the filter.
- The centrifugal separator or cyclone is similar to the inertial impactors. Cyclones commonly are conical or cylindrical in shape, with an opening through which particulate-laden air is drawn along a concentrically curved channel. Larger particles impact against the interior walls of the unit due to their inertia and drop into the base of the separator. The lighter particles continue on through and are drawn up through the separator and collected on a filter. Cyclones can be very compact and thus are often used for personal sampling.

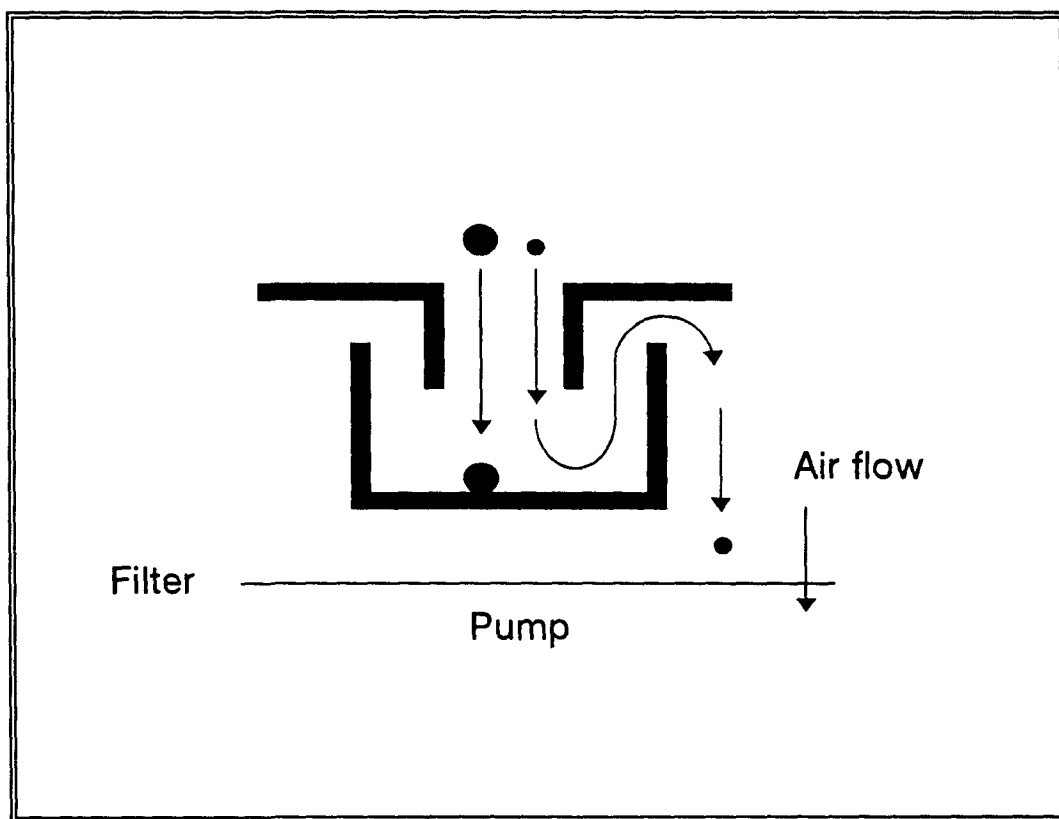


FIGURE 2. ILLUSTRATION OF AN INERTIAL IMPACTOR

- Cascade impactors (**Figure 3**) are composed of a number of stacked perforated collection beds or plates, each with openings narrower than the one before it. The cascade impactor separates particulates in an airstream by directing them toward a dry or coated flat surface. As the particulate-laden air moves through the plates, larger particles are deposited near the top and smaller near the bottom.

One major difference between the cascade impactor and other separators is that it can be used to collect each separate fraction for analysis. The other separators are used to separate the "respirable" fraction for analysis from the "total" mass of particulates.

With all preselectors, the separation efficiency is dependent on flow rate control. A specific flow rate is needed for the device to do proper separation.

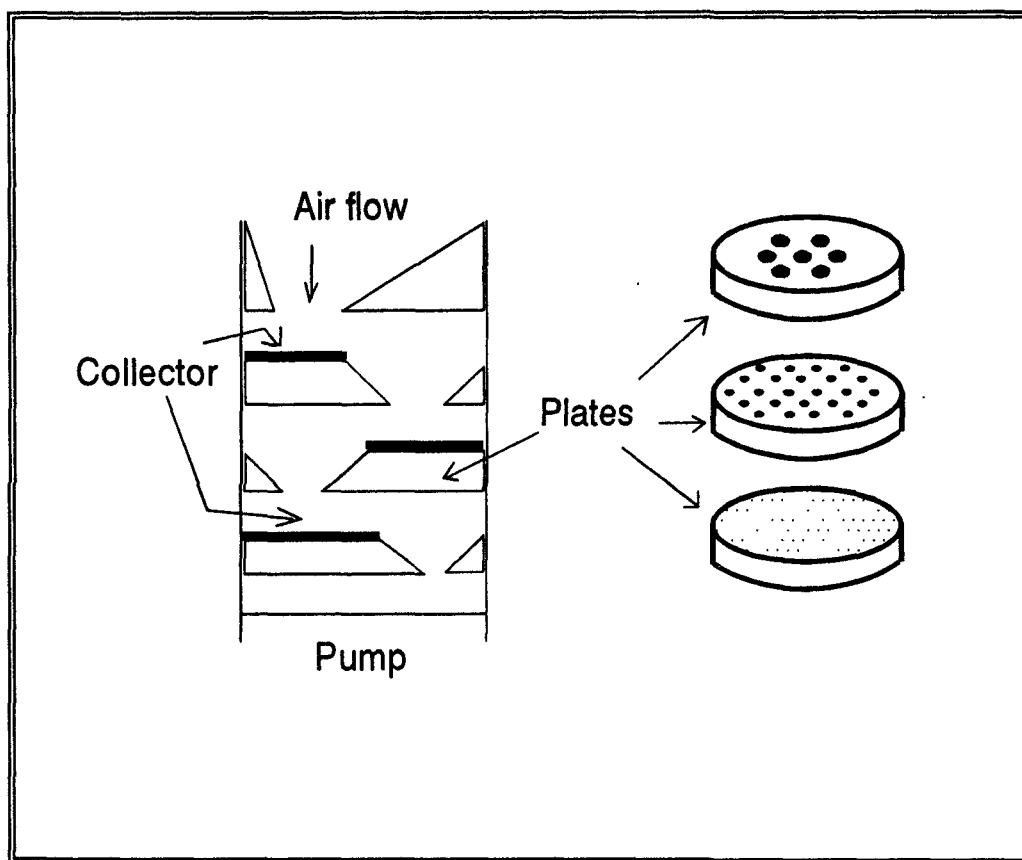


FIGURE 3. CASCADE IMPACTOR

GAS AND VAPOR (VOLATILES) SAMPLERS

Gases and vapors have different physical properties than aerosols and thus would pass through untreated filters without being collected. For gas and vapor collection, a sorbent is needed to separate the contaminant from the atmosphere or a container is needed to collect a whole air sample. The sorbents may be solid or liquid and the containers can be glass, plastic, or metal.

Solid Sorbents

Solid sorbents are a class of media widely used in hazardous materials sampling operations. **Table 2** gives some examples and their applications. These materials collect by sorption and are often the media of choice for insoluble or nonreactive gases or vapors. Their advantages include high collection efficiencies, indefinite shelf lives while unopened, ease of use and specific analytical procedures.

TABLE 2. COMMONLY USED SOLID SORBENTS

Solid Sorbent	Representative Gas or Vapor Adsorbed
Activated charcoal	Nonpolar organics (NIOSH)
Tenax®	Volatile, nonpolar organics (EPA)
Carbon molecular sieve	Highly volatile, nonpolar organics (EPA)
Silica gel	Polar organics (NIOSH)

Sources: NIOSH *Manual of Analytical Methods*, Third Edition, Volume 1, February 1984 and Supplements; EPA's *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA/600/4-89/017, June 1988.

There are several considerations when using solid sorbents. One of the major concerns with the use of solid sorbents is the potential for "breakthrough." Breakthrough occurs when the sorptive capacity of the media is exceeded. There is a limit to the amount of chemical that the sorbent can hold. Most methods limit the volume of air pulled through the sorbent to prevent this problem; hence, the use of low flow pumps for sorbent tube sampling. A way to check for breakthrough is to use a double section tube (**Figure 4**) and analyze each section separately. If a excessive amount of the total sample—one agency uses 25 %—is found in the "back-up" section, then the sample is considered incomplete. Breakthrough is affected by humidity, temperature, total amount of chemicals in air, and the type and amount of sorbent. The problem of breakthrough can be reduced by reducing the air sample volume, increasing the amount of sorbent (e.g., use a 750 mg tube instead of a 150 mg tube) or using tubes in series. For example, the NIOSH methods for vinyl chloride and methylene chloride use two tubes in series.

A sorbent may not be able to collect all of a chemical. The efficiency will vary with sorbent and chemical. That is why there is no universal collection media. The sampling method usually selects the sorbent that will get the highest sorption efficiency (the closer to 100% the better).

Storage and handling of the sorbent samples can also be a problem. They cannot be stored indefinitely. Analysis usually must be done within 2 weeks. Some sorbents require special handling. The EPA method that uses Tenax® tubes for sampling requires the operator to wear cotton gloves so as not to contaminate the media with skin oils. The method requires storage away from sunlight.

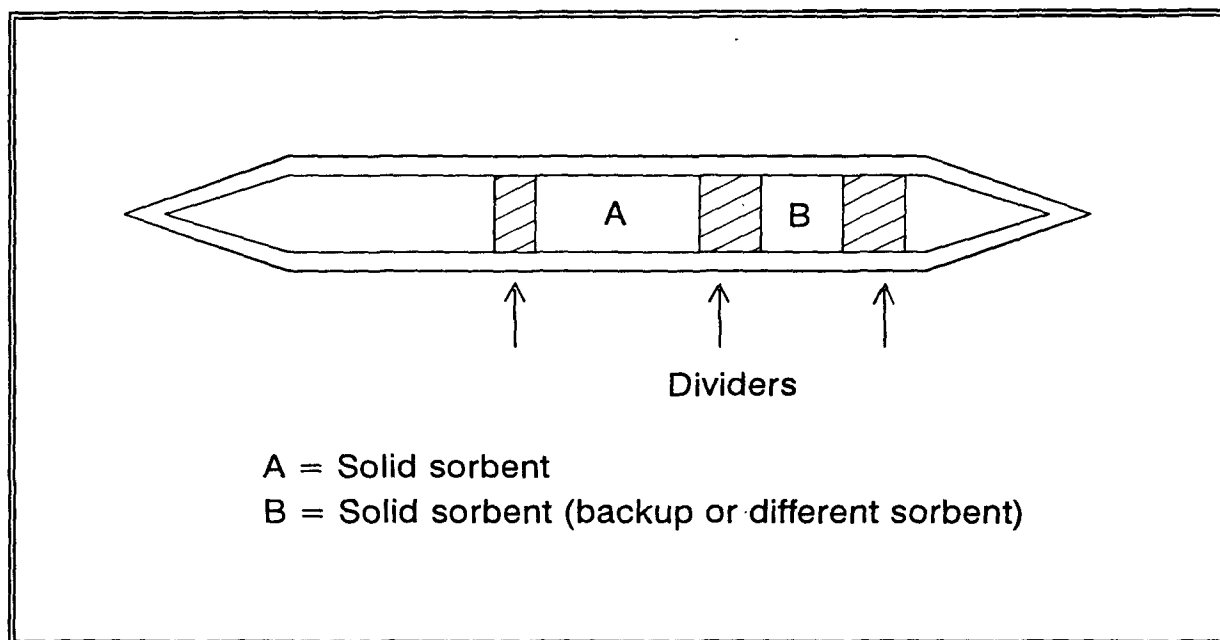


FIGURE 4. TYPICAL 150 MG SOLID SORBENT TUBE

When the samples are analyzed, the chemicals must be desorbed from the media. This can be done with solvents (e.g., carbon disulfide) or with heat (thermal desorption). Solvent desorption can involve hazardous liquids and needs a controlled laboratory environment. Thermal desorption can be done with automated equipment and does not need hazardous chemicals. However, the elevated temperatures may cause a change in some unstable chemicals.

Once the sample is desorbed, it can be analyzed by a variety of detectors.

Liquid Sorbents

Liquid sorbents are used to collect soluble or reactive gases and vapors (**Table 3**). Only a relatively few analytical methods use liquid sorbents. Further, most of the common liquid absorbers tend to be contaminant-specific and have limited shelf lives.

The liquid sorbents need a sampler to hold the liquid during sampling. These samplers ensure that contaminants in the sampled air are completely absorbed by the liquid sampling medium. There are several varieties of samplers. Differences in design are due to the efficiency needed for absorption.

- Impingers, or simple gas washers (**Figure 5a**), are a basic liquid holding sampler. This device consists of an inlet tube connected to a stopper fitted into a graduated vial such that the inlet tube rests slightly above the vial bottom. A measured volume of liquid is placed into the vial, the stopper inlet is put in place, and the unit is then connected to the pump by flexible tubing. When the pump is turned on, the contaminated air is channeled down through the liquid at a right angle to the bottom of the vial. The air stream then impinges against the vial bottom, mixing the air with the liquid and the necessary air-to-liquid contact achieved by agitation. The

TABLE 3. COMMONLY USED LIQUID ABSORBERS

Absorbing Liquid	Gas/Vapor Absorbed
0.1 <i>N</i> NaOH	Cresol/phenol (EPA); phenol (NIOSH)
0.1 <i>M</i> HCl	Hydrazine (NIOSH)
Aniline	Phosgene (EPA)
DNPH reagent and isooctane	Aldehydes/ketones (EPA)

Sources: NIOSH *Manual of Analytical Methods*, Third Edition, Volume 1, February 1984 and supplements; EPA *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA/600/4-89/017, June 1988.

popularity of impingers rests on such qualities as simple construction, ease of cleaning, the small quantity of liquid used (typically less than 25 to 30 milliliters), and a size suitable for use as a personal monitor.

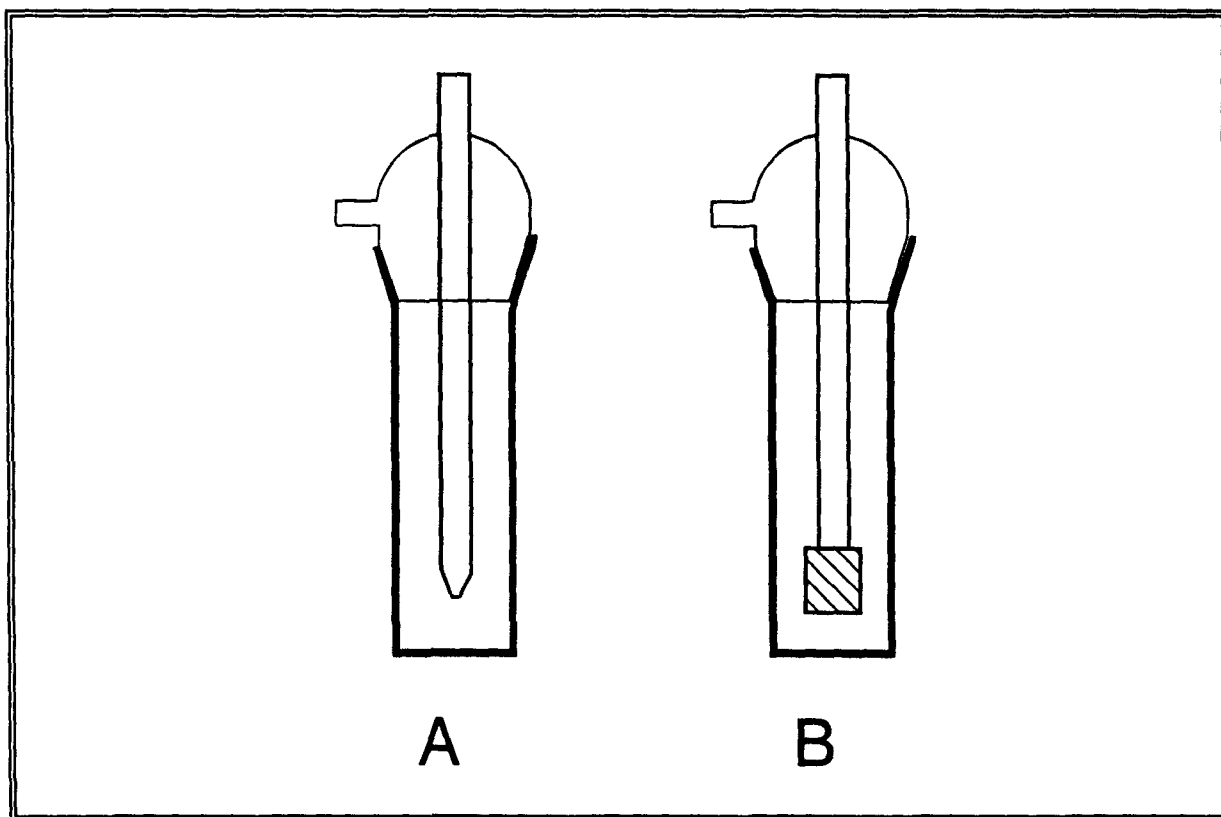


FIGURE 5. A - IMPINGER; B - FRITTED BUBBLER

Source: *The Industrial Environment - Its Evaluation and Control*, NIOSH, 1973.

- Fritted bubblers (**Figure 5b**) are generally used when a high degree of air-liquid mixing is desired. They are similar in construction to the impinger, but have a mass of porous glass, called frits, at the end of the submerged air tube. The frits break the air stream into numerous small bubbles. The frits are categorized as fine, coarse, or extra coarse, depending on the number of openings per unit area. By producing smaller sized bubbles, a greater surface area of the air sample is in contact with the liquid medium.

One of the major disadvantages with liquid sorbent sampling is that the samplers are generally made of glass and, thus, are fragile. Other disadvantages are the need for low, controlled flow rates to prevent overflow of liquid; spillage of liquid if the sampler is worn as a personal sampler; extra handling and storage of liquids; possible evaporation of liquid sorbent during sampling and thus loss of sample; and a need for a safety device (extra impinger, for example) between sampler and pump to prevent liquid contamination of the pump.

Passive Dosimeters

Passive dosimeters now available apply to gas and vapor contaminants only. These devices primarily function as personal exposure monitors, although they have some usefulness in area monitoring. Passive dosimeters are commonly divided into two groups, primarily on how they are designed and operated.

- Diffusion samplers (**Figure 6**) function by the passive movement of contaminant molecules through a concentration gradient created within a stagnant layer of air between the contaminated atmosphere and the collection material.
- Permeation dosimeters rely on natural permeation of a contaminant through a membrane. The efficiency of these devices depends on finding a membrane that is easily permeated by the contaminant of interest and not by other contaminants. Permeation dosimeters are therefore useful in picking out a single contaminant from a mixture of possibly interfering contaminants.

There are liquid and solid sorbents available for passive dosimeters. However, solid sorbents are the most common.

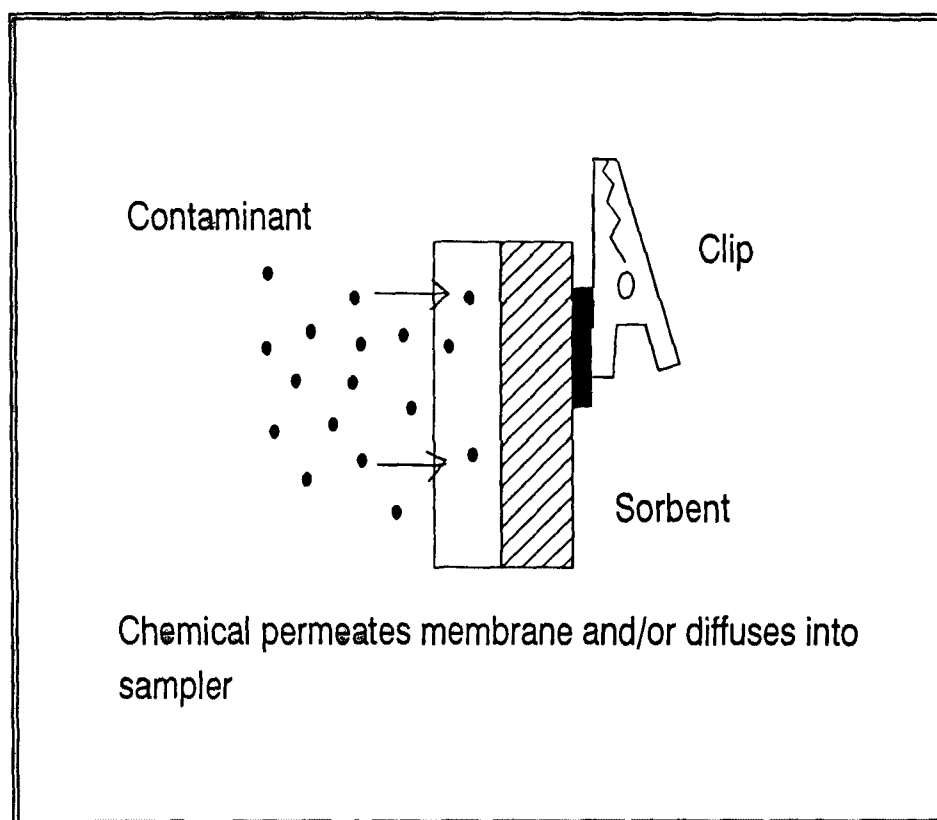


FIGURE 6. DIFFUSION TYPE PASSIVE DOSIMETER

Quantitative passive dosimeters have become available only since the early 1970s, though a semiquantitative passive monitor for carbon monoxide was patented as early as 1927. The key advantage of dosimeters is their simplicity (**Figure 6**). These small, lightweight devices do not require a mechanical pump to move a contaminant through the collection media. Thus, calibration and maintenance of sampling pumps are not needed. However, the sampling period must still be accurately measured. Like active systems, these devices can be affected by temperature and humidity. Sources of error unique to passive dosimeters arise from the need for minimum face velocities and the determination of contaminant diffusion or permeation coefficients.

Container Sampling

Because of the problems associated with sorbent sampling (breakthrough, sorbent efficiency, etc.), methods have been used to collect a whole air sample in a container. Several types of containers have been used.

Glass bottles have been used because of the relative inertness of glass. The procedure can be done several ways. The glass container can be evacuated to produce a vacuum and then opened in the sampling area. While this technique does not use a sampling pump, some way of evacuating the container is needed. Another method uses a pump to pull air through the container. When the air sample has replaced the air in the container, the container is closed. Another device uses a container

filled with water. When the water is drained, the air sample fills the space left by the departing water. This method is undesirable if water vapor is a problem in the analysis.

The devices have two problems. The containers are fragile and only give a sample at ambient pressure. To get a sample out, a vacuum needs to be pulled on the container or air added to equalize pressure as a sample is taken out. As more and more samples are removed, it becomes harder and harder to get the sample out. This also requires a pressure correction when calculating the contaminant concentration. If air is added to equalize pressure, the sample becomes diluted.

Sample collection bags can be constructed of a number of synthetic materials, including polyethylene, Saran™, Mylar™, Teflon™. They are square or rectangular with heat-sealed seams, hose valve fittings, inlet valves, and septums for syringe extraction of samples. They come in a variety of volumes. The selection of a bag should be based on a number of characteristics, including resistance to adsorption and permeation, tensile strength, performance under temperature extremes, construction features (seams, eyelets, and fittings), and intended service life.

Bag sampling can be done by connecting the bag inlet valve with flexible tubing to the exhaust outlet of a sampling pump. The bag inlet valve is opened, the pump turned on, and the sample collected. Once sampling is completed, the pump is turned off, the bag valve closed and the bag disconnected. The bag contents may be analyzed by connecting the bag to a direct-reading instrument; or a portion of the contents can be taken from the bag by a syringe and injected into a gas chromatograph.

In situations where there is concern about sample contamination due to passing through a pump, an alternate sampling apparatus can be constructed. This apparatus involves using the pump to evacuate a chamber (a desiccator or a sealable box) in which the sample bag is installed (**Figure 7**). As the pump creates a partial vacuum, the sample bag expands and draws the sample in through a sample tube.

The major disadvantage of gas sample bags is sample stability. Chemicals in the sample may sorb to the bag material or permeate through the bag walls. This would cause a decrease in sample concentration. The sample can also be affected by contaminants outside the bag by permeation through the bag walls. If a bag is reused, sorbed chemicals may desorb into the new sample and cause contamination. Because of these problems, bags are seldom reused, and samples are analyzed as quickly as possible (usually within 24 hours).

Chemicals in the bag can degrade with exposure to sunlight. The bags should be stored in a container (e.g., a cooler or garbage bag) to prevent exposure to sunlight.

Recently, *metal canisters* have gained popularity. Until recently, there have been problems with reactions occurring with the metal on the insides of the container. New polishing techniques have greatly reduced the problem. Metal canisters are used similarly to glass containers. They are evacuated to produce a vacuum. Unlike glass containers, metal canisters can be filled several ways. The valve can be opened to get a instantaneous, or grab, sample. The canister can also be connected to a controlled flow orifice so that the sample fills the canister at a fixed rate. This gives a long term sample.

A pump can also be used to pressurize the canister so that a sample volume greater than the canister size is obtained. This latter capability is not available for glass containers or gas bags.

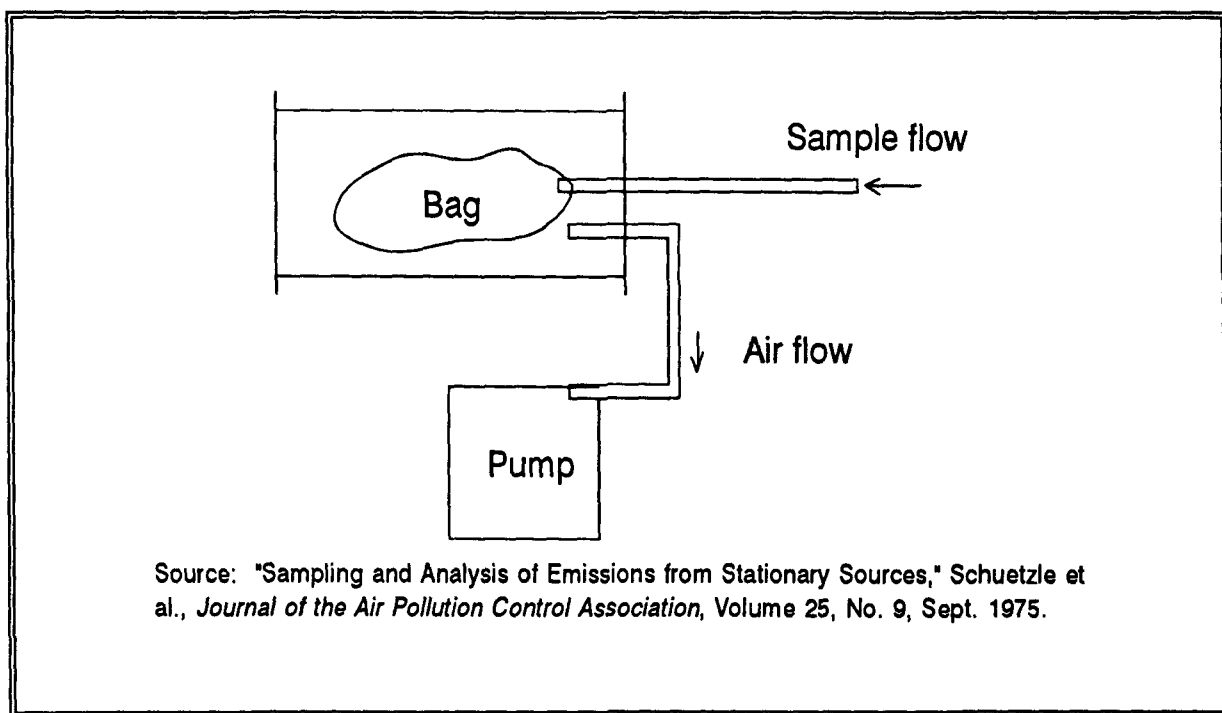


FIGURE 7. NEGATIVE PRESSURE BAG SAMPLING APPARATUS

Metal canisters are more durable than glass containers. They have better sample stability than gas bags. There are special cleaning procedures that allow the canister to be reused.

Metal canisters have a problem with recovery of polar compounds (e.g., alcohols).

Syringes can also be used to take a sample. Although 1-liter syringes are available, most are rather small and there may be a problem with having an adequate amount of sample.

Container sampling allows whole atmosphere sampling. This type of sampler eliminates the problems associated with sorbent media. It also allows the use of more than one analytical method per sample. Glass containers are fairly inert but are fragile. They also are limited in size. Gas bags are more durable and have a variety of sizes, but have sample stability problems. Metal canisters are durable, have good sample stability and can get a larger sample than their actual size (but only if special equipment is used). There are systems for taking personal samples with a gas bag. Gas bags and metal canisters can also obtain long term samples with controlled flow pumps.

SEMIVOLATILE SAMPLERS

Some chemicals, because of their physical properties, may be present in both solid and vapor form. There are also chemicals that are not very volatile, but will vaporize gradually if air is passed over them. This could happen if the chemical was captured on a filter. Because of these situations, some methods use more than one type of media. Usually a filter (for the aerosol phase) is followed by a sorbent (for the vapor phase). **Table 4** gives examples of chemicals that are in this category and the methods used to collect them.

Because two separate media are used, both will probably be analyzed by different methods. It will also take more time and be more expensive for the analysis.

TABLE 4. COMMON MULTIMEDIA SAMPLERS

Media Used	Chemical Being Sampled
0.8- μ m MCE filter + 0.1 N KOH	Cyanides (NIOSH)
13-mm glass fiber filter and Florisil	Polychlorinated biphenyls (PCBs) (NIOSH)
Quartz filter and polyurethane foam (PUF)	PCBs/pesticides (EPA) Polycyclic aromatic hydrocarbons - PAHs (EPA)
Quartz filter + XAD-2	PAHs (EPA)

Sources: NIOSH *Manual of Analytical Methods*, Third Edition, Volume 1, February 1984 and supplements; EPA *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA/600/4-89/017, June 1988.

SAMPLING PUMPS

Pump Characteristics

Air sample collection systems, with the exception of evacuated canisters and passive dosimeters, rely on electrically powered pumps to mechanically induce air movement. The power source may be batteries or an AC source. Battery-powered pumps can operate for 6-10 hours. AC-powered pumps can operate longer, but are not usable as personal samplers.

Generally, sampling pumps incorporate several of the following features:

- A diaphragm or a piston-type pumping mechanism
- A flow regulator to control the sampling flow rate
- A rotameter or stroke counter to indicate flow rate or sample volume
- A pulsation dampener to maintain a set flow rate
- A programmable timer to start the pump at a set time and/or to stop the pump after a set sampling period
- An inherent safety approval for gas/vapor and dust atmospheres

Other than differences in features mentioned above, the main difference in pumps is their flow rate. Low flow pumps have a flow rate range from 10 cubic centimeters per minute (cc/min) to about 750 cc/min. Medium flow pumps have a flow rate of about 1–6 liters per minute (lpm). High volume (Hi-Vol) pumps are AC powered and can achieve up to 40 cubic feet per minute (cfm). That is equivalent to 1130 lpm.

The choice of flow rate depends on the type of sampling done. Sorbent media, like carbon tubes, cannot be used with a high flow rate. The capacity of the sorbent would be exceeded and there would be a loss of sample (breakthrough). Also, the Hi-Vol pumps are not used as personal samplers. Some pumps have the ability to do both low and medium flow sampling, but not Hi-Vol.

Calibration

All pumps must be calibrated. The flow rate must be known so that a sample concentration can be calculated. Calibration is also necessary to ensure the constant flow rate needed for some methods. The flow rate stability of a pump should be accurate to within $\pm 5\%$ of its set flow rate.

An active sampling system must be calibrated prior to and after sampling. The overall frequency of calibration depends upon the general handling and use a system received and the quality control considerations of the user. Pump mechanisms must be recalibrated after they have been repaired, when newly purchased, and following any suspected abuse. The sampling system as a whole must be calibrated to the desired flow rate rather than the pump alone. The sampling system should be calibrated prior to and after each use. The system can be adequately examined under field-like conditions only with all components connected.

There are several devices for calibrating sampling pumps:

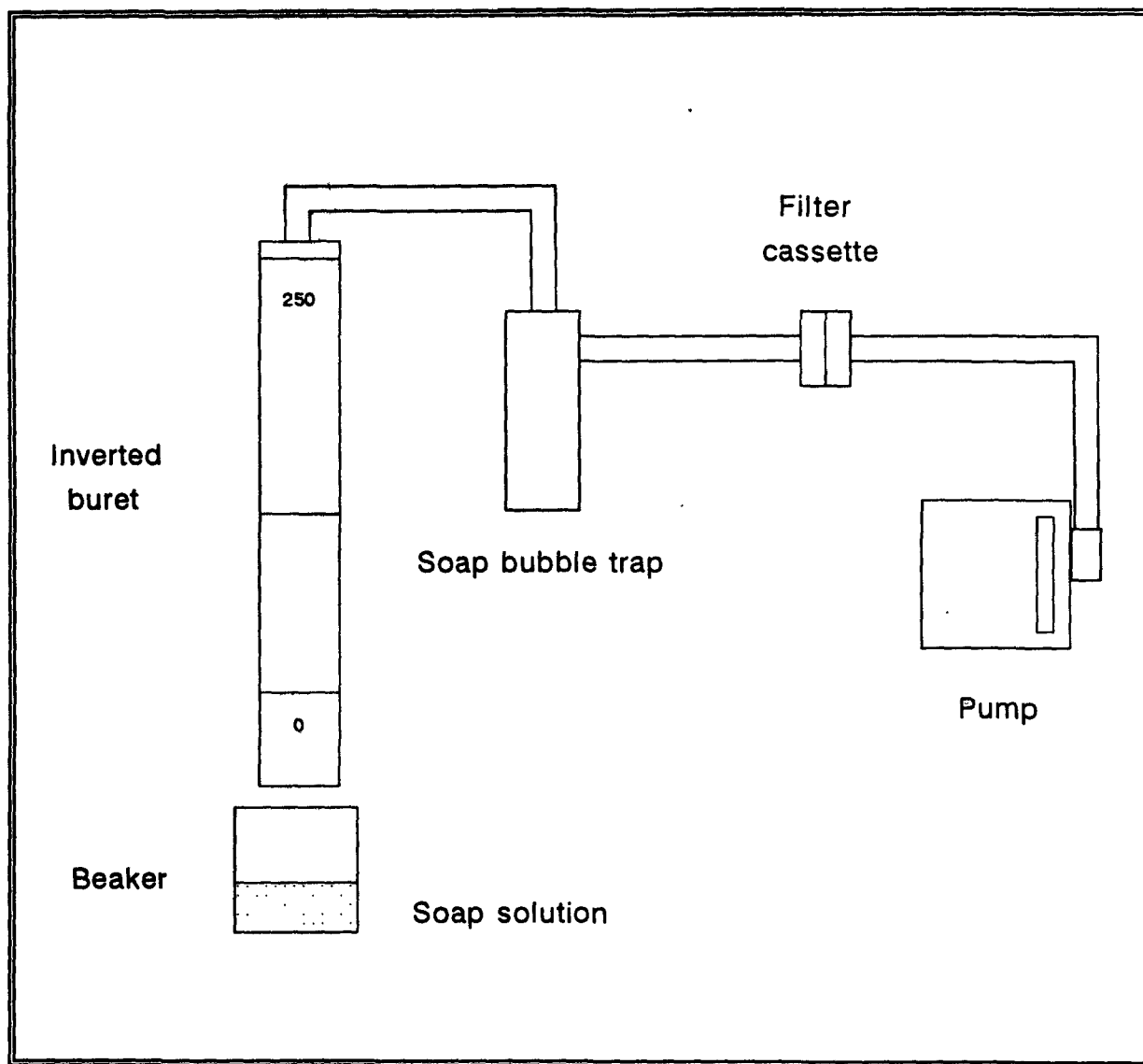
- The soap bubble meter represents a basic method of calibration and is a primary standard. This device typically consists of an inverted graduated burette connected by flexible tubing to the sampling train. **Figure 8** shows one example.

Do the calibration as follows:

- Start the system's pump to create airflow into the burette
- Dip the open end of the burette into a soap solution to create a soap film bubble across the opening
- Remove the solution and allow the bubble to rise up through the burette
- Measure the travel time of the bubble between two graduated points on the burette; vary the flow rate by adjusting the pump flow regulator.

The general formula used for the calculation of the flow rate is:

$$\text{Flow rate} = \frac{\text{volumetric distance traveled by bubble (ml)}}{\text{travel time of bubble (sec)}}$$



**FIGURE 8. CALIBRATION SETUP FOR FILTER SAMPLER
USING A SOAP BUBBLE METER**

Source: *OSHA Technical Manual*, U.S. Department of Labor, OSHA, 1990.

If the desired flow rate is lpm, then the units need to be converted by multiplying the previous equation by the following:

$$\frac{60 \text{ seconds/minute}}{1000 \text{ ml/l}}$$

- There are electronic bubble meters that use sensors to detect the soap bubble and start and stop an electronic timer. The calibrator then automatically calculates and displays the pump flow rate.

- The precision rotameter consists of a vertically mounted tapered tube with a float inside the tube. When attached to an operating pump, the float rises until the rate of flow is sufficient to hold the float stationary. The flow rate is read from markings on the tube at the point the float is stationary. **Figure 9** illustrates a precision rotameter.

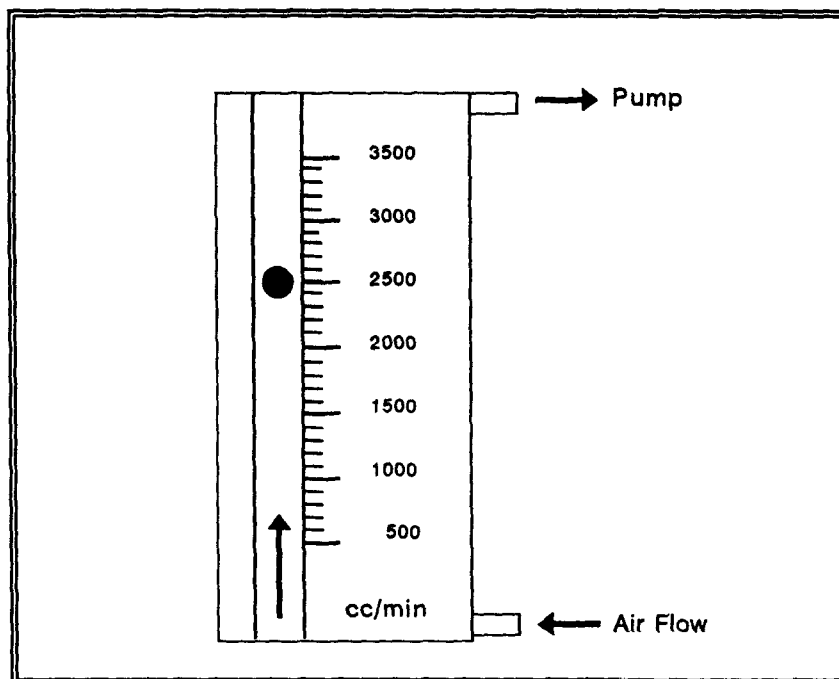


FIGURE 9. EXAMPLE OF A PRECISION ROTAMETER

Whereas the precision rotameter usually is more compact and portable than the soap bubbler meter, it is considered a secondary standard. This means that the rotameter must be checked occasionally with a primary standard such as a bubble meter.

- A manometer is sometimes used to calibrate Hi-Vol samplers because of the high flow rates. A manometer is a tube filled with a liquid. The level of the liquid changes due to pressure changes at the end attached to the sampling pump. A calibration chart is used to convert the change in liquid level to flow rate.

CONCLUSION

When taking air samples for laboratory analysis, several factors need to be considered. Sampling and analytical methods have been developed for many chemicals by several agencies that have looked at these considerations. The *References* section provides a list of references on air monitoring and sampling.

APPENDIX A

Air Sampling Methods Database



United States
Environmental Protection
Agency

Office of
Solid Waste and
Emergency Response

January 1993

Air Sampling Methods Database

Office of Emergency and Remedial Response
Emergency Response Division

Technical Bulletin
Volume 1, Number 1

What is the Air Sampling Methods Database?

The Air Sampling Methods Database is a PC-based software package which allows its users to access summarized standard methods for chemical analysis. The program, which was designed to be used in conjunction with the Representative Air Sampling Guidance for the Removal Program document, formulate sampling plans to give the best possible site characterization. This allows users to make quick determinations about which methods are most appropriate to use and which best suit their informational needs in order to plan a sampling event that most aptly depicts the objectives of a particular site investigation.

The user can search the software by method name and number, chemical name, or Chemical Abstracts Number (CAS #). The method summary can be viewed and the method marked for printing. Furthermore, the software can be tailored to its users since they have the capacity to input their own user-developed methods into the database without affecting the established standardized methods. Users can submit supporting documentation for their methods to the United States Environmental Protection Agency's Environmental Response Team (U.S. EPA/ERT) for possible permanent inclusion to the database.

Who Are the Anticipated Users?

On-Scene Coordinators (OSC), Technical Assistance Team (TAT) members, Emergency Response Contractors (ERCs), site Health and Safety air personnel, and U.S. EPA air plan reviewers are the primary users of the Air Sampling Methods Database. By using the program, these individuals gain access to the sampling objectives which best characterize a site. Then, users can assimilate this information into an acceptable repre-

sentative sampling program. The Air Sampling Methods Database also can aid any U.S. EPA personnel or agency that performs air monitoring at hazardous waste sites.

Why Was the Air Sampling Methods Database Designed?

The Air Sampling Methods Database was created to expand the knowledge base during remedial emergency response actions. It gives insight to two major criteria for preparation of a representative air sampling plan: selecting the appropriate air sampling approach and choosing the proper equipment to collect and analyze a sample. Timely decisions regarding health and safety and acute health risks can be made by utilizing these summarized methodologies:

- National Institute of Occupational Safety and Health (NIOSH) 2nd and 3rd Edition Methods.
- Occupational Safety and Health Administration (OSHA) Methods.
- Selected American Society of Testing and Materials (ASTM) Methods. Volume 11.03 Atmospheric Analysis; Occupational Health and Safety.
- EPA Toxic Organic Compounds Methods.
- Contract Laboratory Program - Statement of Work Methods.
- Indoor Air Compendium Methods.
- Code of Federal Regulations (CFR) Methods.

This facilitates a greater variety of options for the users, who then can select the appropriate air sampling objectives and plans that best suit the needs of a particular assignment.

Features of the Air Sampling Methods Database

- Is user friendly.
- Requires no other software for support (self-contained).
- Adds, deletes, and edits methods added by a user.
- Traces information by on-line references.
- Provides single point of update.
- Gives semi-annually updates.
- Allows access to update information available via Environmental Response Center (ERC), Office of Solid Waste and Emergency Response (OSWER), U.S. EPA/ERT, and Dataport bulletin boards by modem.
- Generates hard copy.

Future Features:

- Hot-Key on-line help.
- Hot-Key on-line glossary of terms.

- 50-100 word text summaries discussing sampling trains, flow rates, interferences, detection limits, analysis information, etc.
- Synonym searching of chemical names.

Requirements

To run the Air Sampling Database, you must have the following:

- An IBM PC or IBM-compatible computer
- A hard drive
- 640K RAM
- A printer (for hard copy output)

For more information about the Air Sampling Database, contact:

*Mr. Thomas Pritchett, Phone: (908) 321-6738
U.S. Environmental Response Team
2890 Woodbridge Ave
Building 18, MS-101
Edison, New Jersey 08837-3679*

INTRODUCTION TO GAS CHROMATOGRAPHY

PERFORMANCE OBJECTIVES

At the end of this lesson, participants will be able to:

- List the components of a gas chromatograph
- Define retention time
- List the factors that affect retention time
- Name the two types of columns and describe their differences.

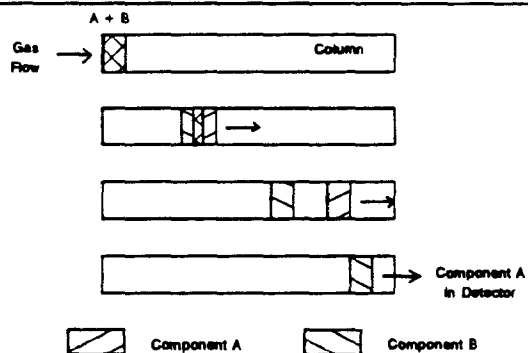
INTRODUCTION TO GAS CHROMATOGRAPHY

GAS CHROMATOGRAPHY Definition

A technique for separating volatile substances in a mixture by percolating a gas stream over a stationary phase

Source: *Basic Gas Chromatography*

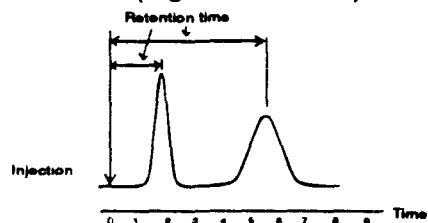
SEPARATION OF A MIXTURE BY GAS CHROMATOGRAPHY



NOTES

RETENTION TIME Definition

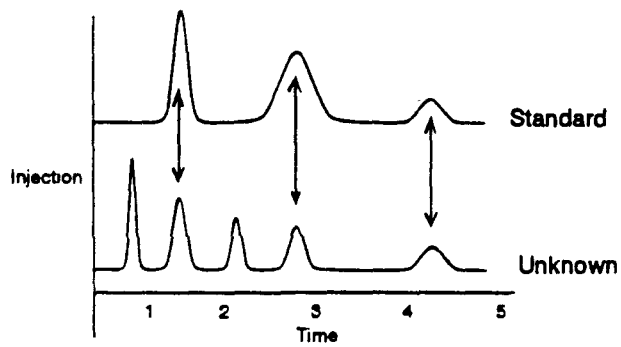
Retention time is the time from sample injection to peak maxima (signal maxima)



RETENTION TIME Application

Used for qualitative identification of chemicals by comparing the retention time of an unknown chemical with retention times of known (standard) chemicals

RETENTION TIME Peak Comparisons



FACTORS AFFECTING RETENTION TIME

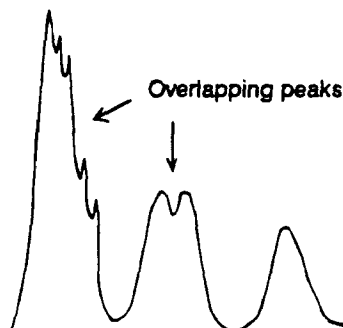
- Column
 - Type
 - Temperature
 - Length
- Carrier gas flow rate

EFFECT OF COLUMN TYPE AND TEMPERATURE

Chemical	Temperature (°C)	Retention Time (min.)	
		G-8 Column	T-8 Column
Benzene	0	1:19	1:43
	40	0:25	0:32
Carbon tetrachloride	0	1:24	0:37
	40	0:25	0:17

Source: The Foxboro Company Chromatographic Column Guide for the Century OVA, 1989

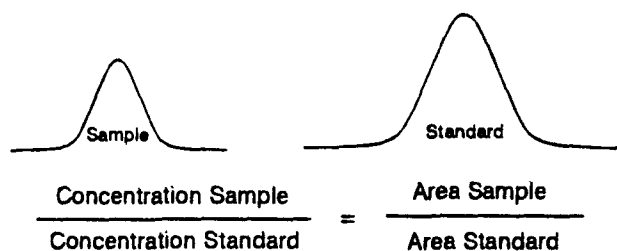
PEAK RESOLUTION Problems



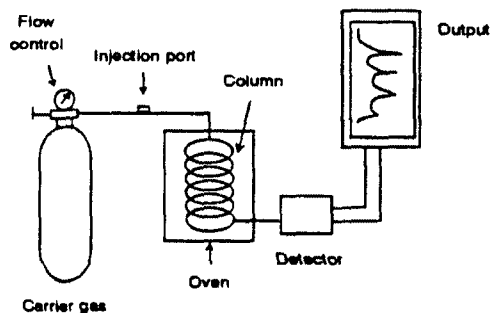
NOTES

PEAK AREA Application

Peak area is used to quantify chemical



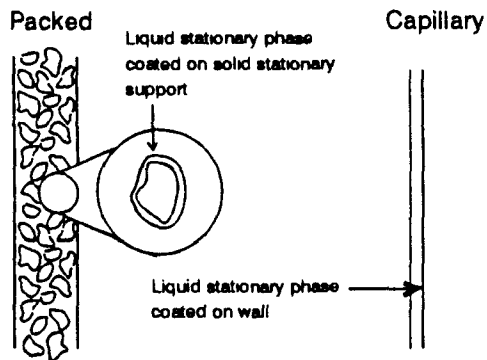
GAS CHROMATOGRAPH Components



CARRIER GAS Characteristics

- Suitable for detector
- High purity
- Does not interfere with sample

GAS CHROMATOGRAPH Columns



COLUMN TEMPERATURE

- Ambient
 - Variable
- Isothermal
 - Constant temperature
- Temperature programming
 - Temperature increases over time

DETECTORS USED IN PORTABLE GCs

- Common detectors
 - Flame ionization detector (FID)
 - Photoionization detector (PID)
- Specialized detectors
 - Thermal conductivity detector (TCD)
 - Argon ionization detector (AID)
 - Electron capture detector (ECD)

NOTES

SPECIALIZED DETECTORS

Why Are They Used?

One detector may be more sensitive than another for certain compounds.

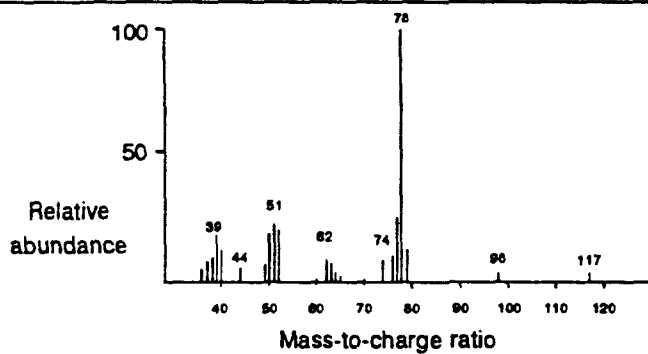
e.g. The ECD is best detector for halogenated compounds.

MASS SPECTROMETER

- Chemical exposed to electrons
- Molecule or fragments are ionized
- Ions separated by magnetic field
- Separation based on speed and mass-to-charge ratio
- Only detector capable of providing additional compound identification beyond retention time

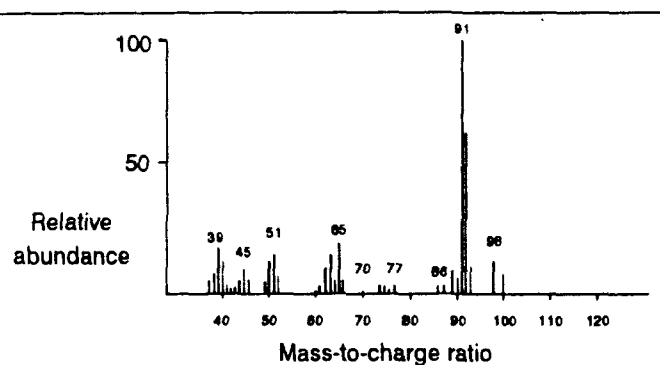
MASS SPECTRUM

Benzene



NOTES

MASS SPECTRUM Toluene



GAS CHROMATOGRAPHY Field Applications

- Air analysis
- Field screening
- Soil gas

SUMMARY

- Gas chromatography is used to identify and quantify chemicals
- Qualified operators are needed
- Right tool for the job?

INTRODUCTION TO GAS CHROMATOGRAPHY

INTRODUCTION

Gas chromatography is a separation technique wherein components of a sample are separated by differential distribution between a gaseous mobile phase (carrier gas) and a solid (gas solid chromatography) or liquid (gas liquid chromatography) stationary phase held in a column. The sample is injected into the carrier gas as a sharp plug and individual components are detected as they come out ("elute") of the column at characteristic "retention times" after injection. **Figure 1** illustrates this concept with a two component mixture.

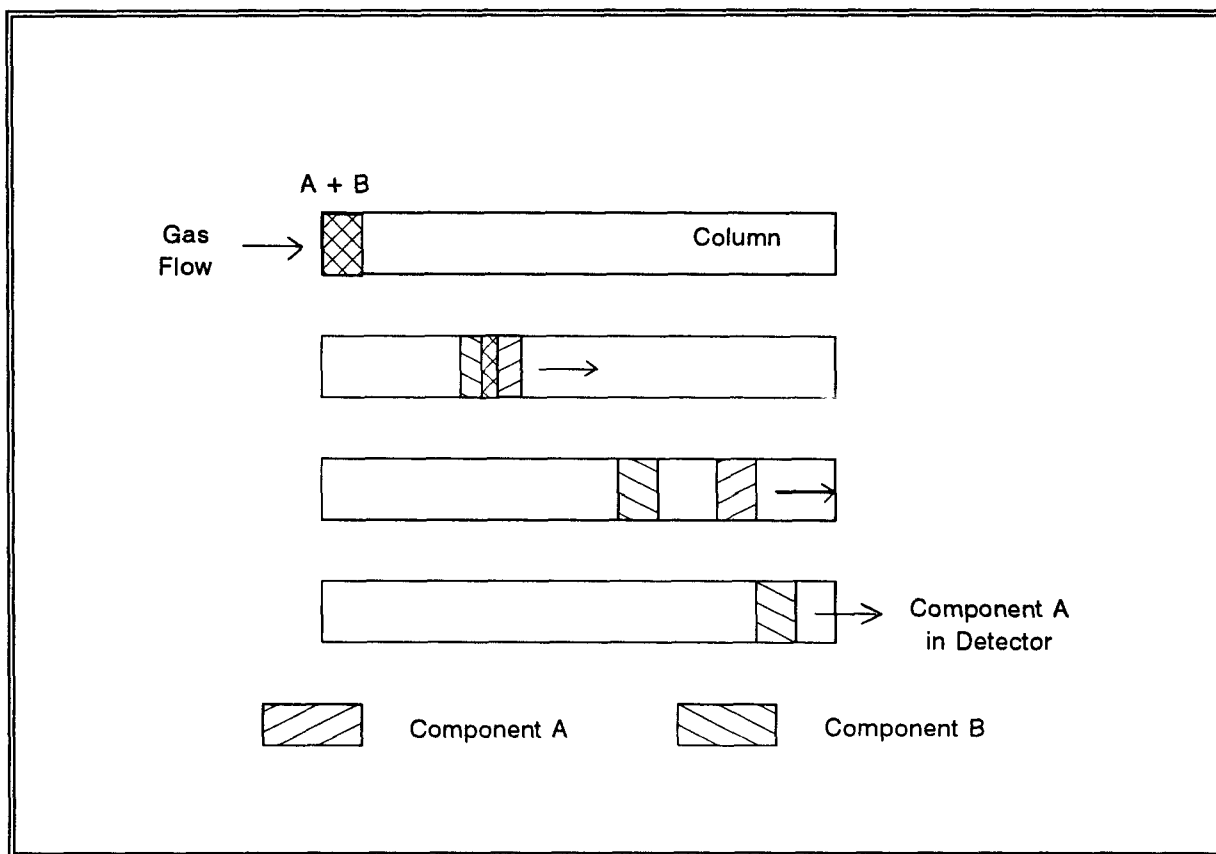


FIGURE 1. SEPARATION OF A TWO COMPONENT MIXTURE BY GAS CHROMATOGRAPHY

As different components elute from the column, they pass through a detector which generates a response (or "peak") based upon the amount of each compound present and upon the sensitivity of the detector. The signal vs. time plot is called the "chromatogram."

QUALITATIVE ANALYSIS

If the temperature of the column and the flow rate of the carrier gas are constant, compounds will elute from the column at a characteristic time (retention time). The retention is characteristic of the compound and the type of column used. Retention time is the time from injection of the sample to peak response of the detector to the eluted compound (**Figure 2**).

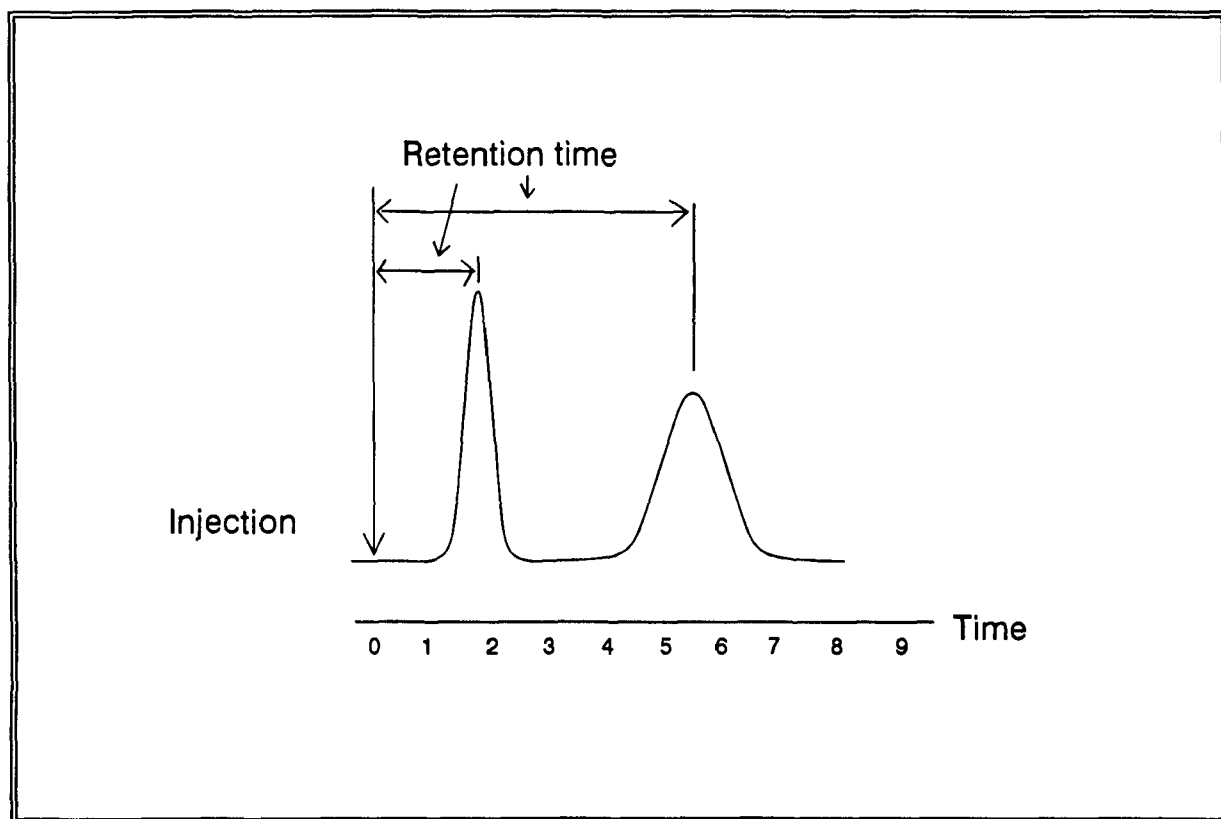


FIGURE 2. CHROMATOGRAM ILLUSTRATING RETENTION TIME

Qualitative analysis can be done by comparing the retention times of the compounds in an unknown sample with the retention times of known compounds in a standard analyzed under identical conditions. **Figure 3** shows a comparison of a sample with a standard.

Retention Time

Retention times are governed by several factors:

1. The type of column used. Different packings and liquid coatings change retention time.
2. The column temperature. As the column temperature increases, the retention time decreases. This is why temperature controls are used to keep the column temperature constant.

3. The column length. Double the column length and double the retention time.
4. The carrier gas flowrate. Double the flowrate and halve the retention time.

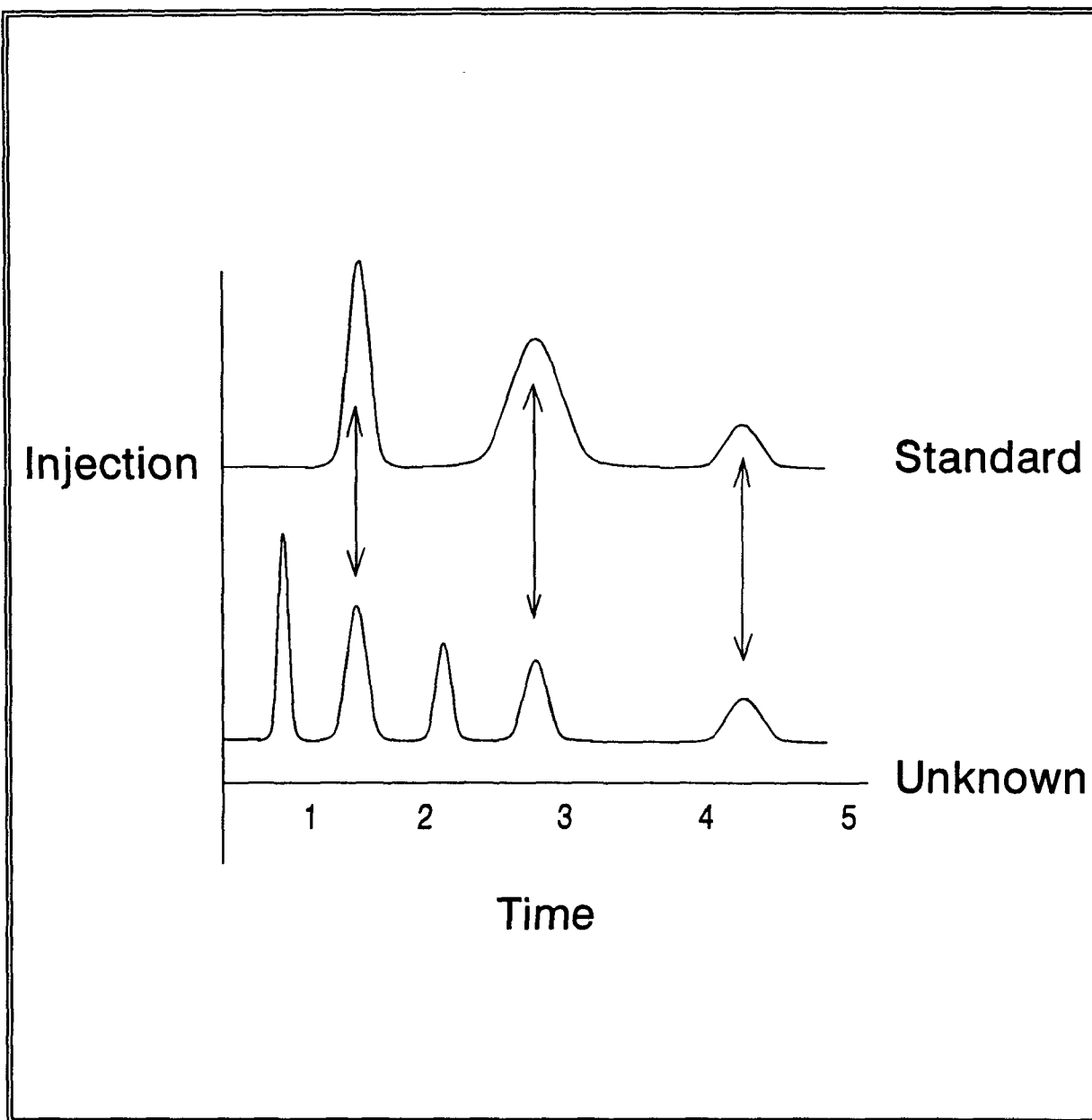


FIGURE 3. EXAMPLE OF A GC CHROMATOGRAM AND THE USE OF RETENTION TIMES TO IDENTIFY COMPOUNDS

Resolution

Resolution, or relative peak width, governs the number of discrete, detectable components of a sample that can be identified and quantified during the GC run. Resolution is governed by:

1. The type of column. Capillary columns have much greater resolution (narrower peak widths) than a packed column.
2. Column length. The longer the column, the narrower the peak width at a given retention time. However, with ambient temperature GCs, increasing the column length will increase the retention times.
3. The carrier gas flowrate. There exists an optimum value for peak resolution. Increasing or decreasing the flowrate from this optimum will widen the peaks.

A problem with poor resolution is co-eluting and overlapping. If two chemicals elute at the same time—co-elute—identification is hindered. If peaks overlap, quantitation of the compounds is difficult. **Figure 4** illustrates overlapping peaks.

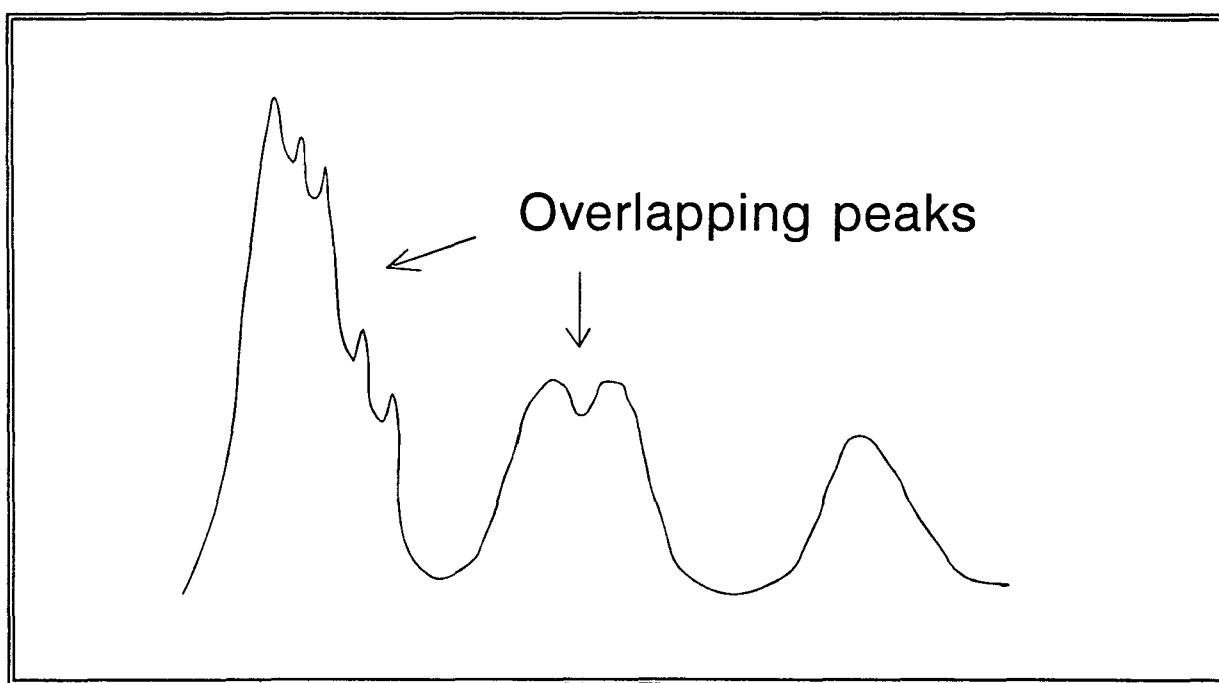


FIGURE 4. EXAMPLES OF OVERLAPPING PEAKS

QUANTITATIVE ANALYSIS

Signal Output

The size of the chromatogram peak for a specific compound is proportional to the amount of chemical in the detector. Quantitative analysis is done by comparing the peak size of the sample compound with the peak size of a known amount of the compound (the standard). The peak size can be quantified in several ways.

Planimetering

Planimetering uses a planimeter to trace the peak. A planimeter is a mechanical device that measures area by tracing the perimeter of the peak. The area is presented digitally on a dial. This method is considered tedious, time-consuming, and less precise than other methods.

Peak Height

Peak height compares the height of the sample compound with the height of the standard. This is a quick and simple method for quantitation. However, peak heights and widths are dependent on sample size and sample feed rate.

Height \times Width at Half-Height

The *height \times width at half-height* uses the height of the peak times the width of the peak at the half-height of the peak. The normal peak base is not used because large deviations may be caused by peak tailing.

Triangulation

Triangulation (**Figure 5**) transforms the peak into a triangle using the sides of the peak to form the triangle and the baseline to form the base of the triangle. The area of the peak is calculated using $\text{Area} = 1/2 \text{ Base} \times \text{Height}$.

Integrators

Peak height, height \times width at half-height, and triangulation are done manually using the chromatogram and a pencil and straight edge. *Integrators* calculate the peak size electronically and record the output. Because of ease of operation, integrators are most frequently used in portable GCs.

When a microprocessor is used, the retention times of the compounds in the sample are compared to the compounds in the standard and the readout identifies the compounds in the sample. Quantitative analysis is done by an integrator. If a compound has been identified, the peak size in the sample is compared to the peak size of the compound in the standard and a sample concentration is given. Thus, the sample is evaluated both qualitatively and quantitatively.

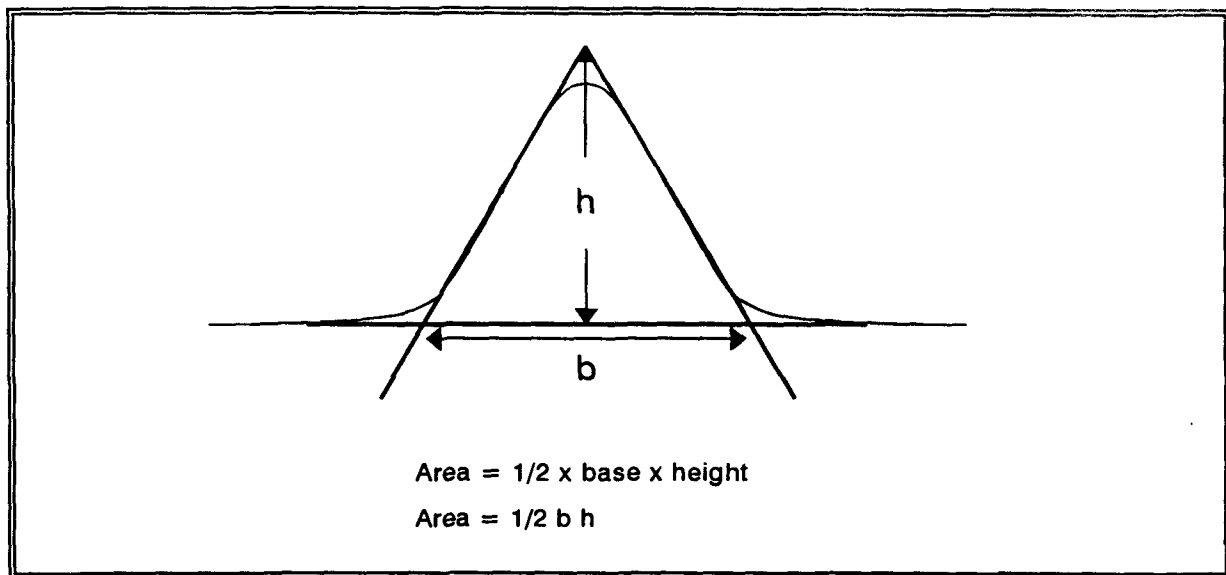


FIGURE 5. MEASUREMENT OF AREA BY TRIANGULATION

Source: *An Introduction to Gas Chromatography*, National Training Center, Water Program Operations, U.S. Environmental Protection Agency, Cincinnati, OH.

COMPONENTS OF A GAS CHROMATOGRAPH

A gas chromatograph (GC) consists of (Figure 6):

- A carrier gas
- A flow control for the carrier gas
- A sample inlet or injector
- A column
- A temperature control for the column
- A detector
- A recorder.

Carrier Gas

A high pressure gas cylinder serves as the source of the carrier gas. The carrier gas should be:

1. Inert to avoid interaction with the sample or solvent
2. Able to provide a minimum of gaseous diffusion
3. Readily available and of high purity
4. Inexpensive
5. Suitable for the detector used.

Commonly used gases are helium, nitrogen, and hydrogen.

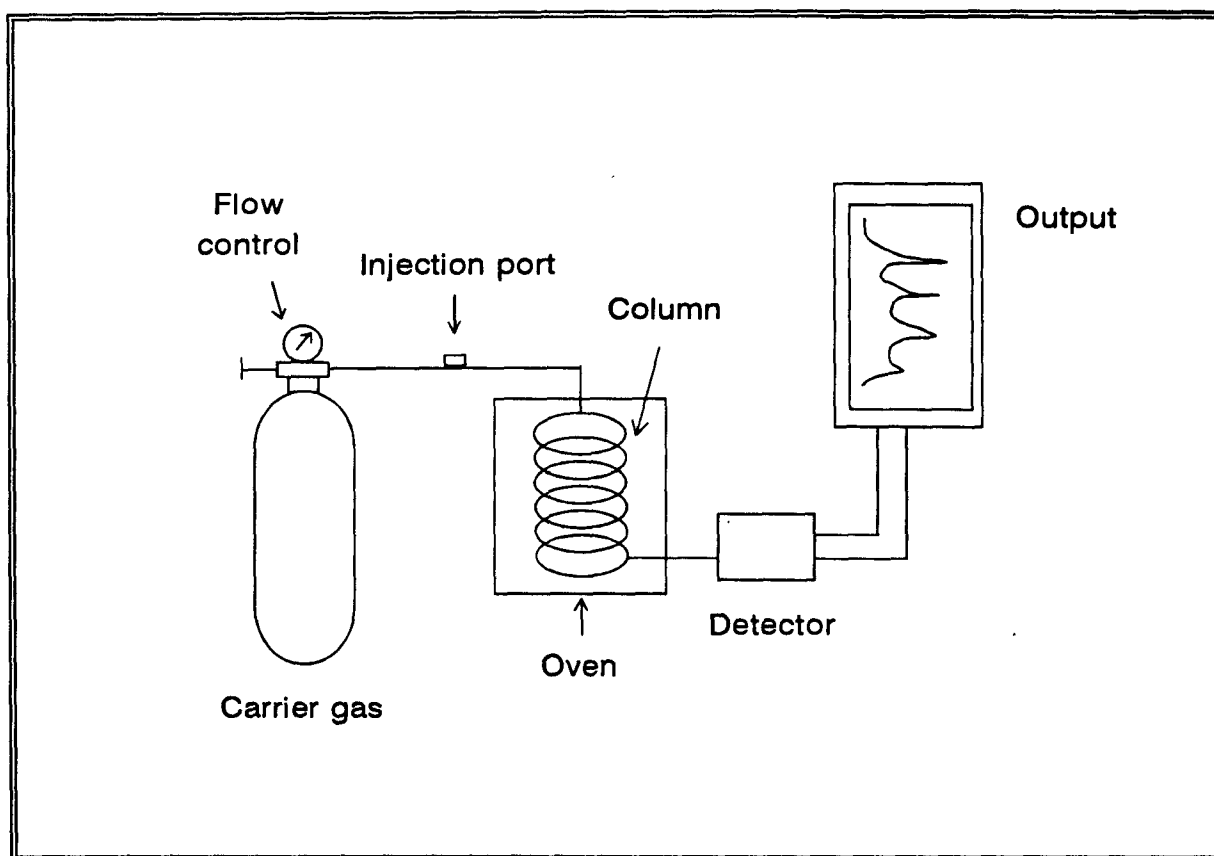


FIGURE 6. COMPONENTS OF A GAS CHROMATOGRAPH

Source: *The Industrial Environment - Its Evaluation & Control*, 1973, National Institute for Occupational Safety and Health.

Portable gas chromatographs (GCs) have internal cylinders that usually have an 8- to 10-hour gas supply. Many of these also have connections for external cylinders to provide longer duration analysis.

Flow Control

Because compounds elute at a characteristic time (retention time) based on a given temperature and a constant flow rate, carrier gas flow control and column temperature are important. A flow controller is necessary to maintain a constant flow rate.

Sample Injection System

Samples are introduced into the column as a single sharp plug. The sample injection system allows introduction of the sample rapidly and in a reproducible manner. Samples can be manually injected by a syringe. Syringe injection allows the operator to control the sample volume. Some GCs have a built-in sample loop that injects a known and consistent volume by manual operation or automatic

programming. Sample volume is important in that the quantitative evaluation of a chromatogram is affected by the sample volume. Also, some columns are limited by the size of sample that can be injected onto them.

Column

The column is a tube made of stainless steel, glass, aluminum, or Teflon®. *Packed columns* contain a solid adsorbent (gas-solid chromatography) or an inert solid support coated with liquid stationary phase (gas-liquid chromatography). *Capillary columns* consist of a liquid stationary phase coated to the inside wall of a thin tube. Gas-liquid chromatography columns and capillary columns are the more common types for the portable GCs.

Tube sizes range from 0.5- to 6-mm outside diameter and from 20 cm to 50 m in length. Capillary columns are usually longer than packed columns. Portable GC columns are typically 4 m in length. Columns can be coiled to fit inside portable units.

Capillary columns give better resolution than packed columns. However, they require smaller injection volumes than packed columns and thus need sample inlets and detectors that can handle small volumes.

Temperature Control

Column temperature affects the retention time of a chemical. A constant temperature is desired to ensure comparison of sample and standards. Temperature control can be:

- *Ambient temperature control*—The column temperature is the same as ambient air. As ambient temperature changes, the retention times change. Consequently, frequent calibration checks are needed. Ambient temperature limits use to volatile compounds. The time to run a sample is longer and thus limits the number of samples that can be run per day.
- *Isothermal temperature control*—The column temperature is maintained at constant temperature by an oven. Retention times are much more stable. Temperatures can be adjusted to reduce analysis time or expand the range of compounds that can be analyzed. Retention times are halved for every 30°C increase in temperature. Isothermal temperature control consumes more electricity than ambient.
- *Temperature programming*—Column temperature is slowly increased under very controlled conditions. This allows simultaneous analysis of compounds with a wide range of boiling points. A lower temperature is used for the volatile components. The temperature is raised to elute the less volatile compounds. More electrical power is needed for this operation.

Temperature control can also be used on the injector and the detector. Heating the injector prevents condensation of the sample (if a vapor) or can ensure vaporization of a liquid sample. The detector may need to be heated to prevent chemical condensation.

Detector

There are a variety of detectors available for GCs. *Flame ionization detectors (FID)* and *photoionization detectors (PID)* are frequently used. Characteristics of these two detectors are discussed in the *Total Vapor Survey Instruments* section. Other detectors include:

- *Thermal conductivity detector (TCD)*—This detector is based on the principle that a hot object will lose heat at a rate that is dependent on the composition of the surrounding gas. When a compound enters the detector, there is a change in the thermal conductivity of the carrier gas. Its advantage is that it is a universal detector for noninert gases and all organics. Its drawback is limited sensitivity—ppm levels. Preconcentration of samples has been used to offset this limitation.
- *Electron capture detector (ECD)*—A radioactive source is used to ionize the carrier gas. Secondary electrons are produced and an electrical current flows between the electrodes in the detector. When a separated compound which has an affinity for the slow electrons enters the detector, electrons are captured with a resultant decrease in electrical current in the detector. This decrease of current is a function of the concentration of the electron capturing compound.

The detector is especially selective for polyhalogenated (e.g., pesticides) and nitro compounds. It has a high sensitivity—mid ppb to high ppt. Sensitivity is a direct function of halogen atoms per molecule.

Its main limitation is that a radioactive source (tritium or nickel-63) is needed, which requires a Nuclear Regulatory Commission (NRC) license.

- *Argon ionization detector (AID)*—Argon ionization detector depends upon two reactions: the excitation of argon to its metastable state by electron bombardment and the ionization of vapor molecules by the transfer of energy from the metastable atoms. When an ionization chamber contains argon and a source of free electrons, the addition of vapor causes an increase in current flow. The current flow change is detected and used as the signal for the presence of the compound in the sample.

Ionization is caused by a radioactive source. As with the ECD, an NRC license is required for use of the radioactive source.

The reaction of the metastable argon atoms with the vapor molecules applies to all molecules with an ionization potential equal to, or less than, the stored energy of the metastable atoms, which is 11.7 eV.

- *Mass Spectrometer (MS)*—In an MS, the chemical is first exposed to a source of electrons. The molecules or fragments are ionized. The ions are passed through a magnetic field. The magnetic field separates the ions based on their speed and mass-to-charge ratio. The ions are collected and a mass spectrum is produced showing the relative abundance of each type of ion. Each chemical has a distinctive mass spectrum. Thus, this detector is the only one listed here that is capable of providing additional compound identification beyond retention time.

Recording Devices

A device is needed to record when a signal is produced in the detector and to record the strength of that signal. A plot of signal vs. time is called a chromatogram. The chromatogram is used for qualitative and quantitative analysis of the sample. Integrators and microprocessors can be used to electronically evaluate the chromatogram.

Power Supply

A power supply is needed to operate the detector, recorder, oven, and additional electronics of the gas chromatograph. To make them portable, field portable GCs usually have a built-in rechargeable battery supply. If only using the battery, time of operation is limited to 8–10 hours. These units are also designed to operate off AC power sources. A few field GCs only operate on AC power.

APPLICATIONS

Portable gas chromatographs allow analysis in the field. Although the results may not be as accurate and precise as a laboratory GC analysis, they can be used for screening purposes. This can reduce the number of samples that need to be handled by a more sophisticated (and more expensive) analysis.

Ambient Air Analysis

Portable GCs can analyze ambient air samples through several methods. Some units can be taken to the area where the sampling is required and an analysis can be performed on the spot. Some units can be programmed to do periodic sampling and store the chromatograms for later retrieval. Newer units can do continual total vapor monitoring and run a sample if the total vapor reading exceeds a designated level. The GC can also be set up in a more stable environment, and grab samples (e.g., a Tedlar bag of ambient air) can be brought to the GC for analysis.

Sample Screening

Soil and water samples can be screened for further analysis by doing headspace sampling. Headspace sampling involves drawing a sample from above the surface of a liquid or soil in a container. The sample is usually drawn with a small syringe which is also used to inject the sample into the GC.

Soil Gas

Gas chromatography can be used to screen soil gas samples. Dissolved volatile organic compounds have a tendency to partition into the atmosphere between the soil particles. By sampling this atmosphere, underground contamination can be tracked.

EXAMPLES OF PORTABLE GAS CHROMATOGRAPHS

The Foxboro Company

The Foxboro Century organic vapor analyzer (OVA) is the instrument described in the *Total Vapor Survey Instruments* section. The OVA-128GC is equipped with a column. The detector used is an FID. The column is at ambient temperature unless an optional temperature pack is used. The portable isothermal pack allows column temperatures of 0°C, 40°C and 100°C. The unit can be purchased with an external recorder/plotter. The company does not supply an integrator, but there are models from other suppliers that can be used.

Photovac International, Inc.

The Photovac series of GCs use photoionization detection. The temperature of the column is controlled by an oven. The currently available models (10S50, 10S70, 10S Plus, Snapshot) have a built-in microprocessor that aids in calibration and handles compound identification and quantitation. These units can be programmed for automatic sampling. The 10S Plus can be programmed to do total vapor monitoring and to do an analysis if an action level is reached. Options include a telephone connection for transferring data from the instrument to a computer and for notifying the user of unusual results during remote monitoring.

Sentex Sensing Technology, Inc.

The Sentex Scentograph is capable of using an AID or an ECD. One of the most notable features of the Scentograph is that a lap-top computer is used for handling the data. This gives a more graphic visual display of the chromatogram and makes operator use easier because of the normal size keyboard. The GC can do automatic functions. It has a temperature controlled column. There is the capability of concentrating the sample before injection. The air sample is pulled through and collected on a sorbent. The sample is then desorbed and injected using a smaller volume than was pulled through the sorbent. A primary consideration with the Scentograph is that, if an AID or an ECD is used, a radioactive source is needed and thus an NRC license is required. A PID and TCD are also available.

The Sentex Scentoscreen is similar to the Scentograph except it uses a PID and can also do total hydrocarbon analysis. It can be switched to an AID/ECD, but can not do total hydrocarbon readout with those detectors.

HNU Systems, Inc.

The HNU Systems' Model 311 is available with a PID or an ECD for its detector. The unit has a microprocessor for data handling. The instrument does not have a battery supply and thus, needs a line power or a portable generator.

Microsensor Technology, Inc.

Microsensor Technology's M200 Microsensor Gas Analyzer uses a TCD. Although this is a more universal detector, it suffers from poor sensitivity. A preconcentrator has been developed and used to reduce this limitation. The more notable characteristic of the M200 is that it sends a sample through two columns at the same time. This gives a better chance of correctly identifying the compounds present.

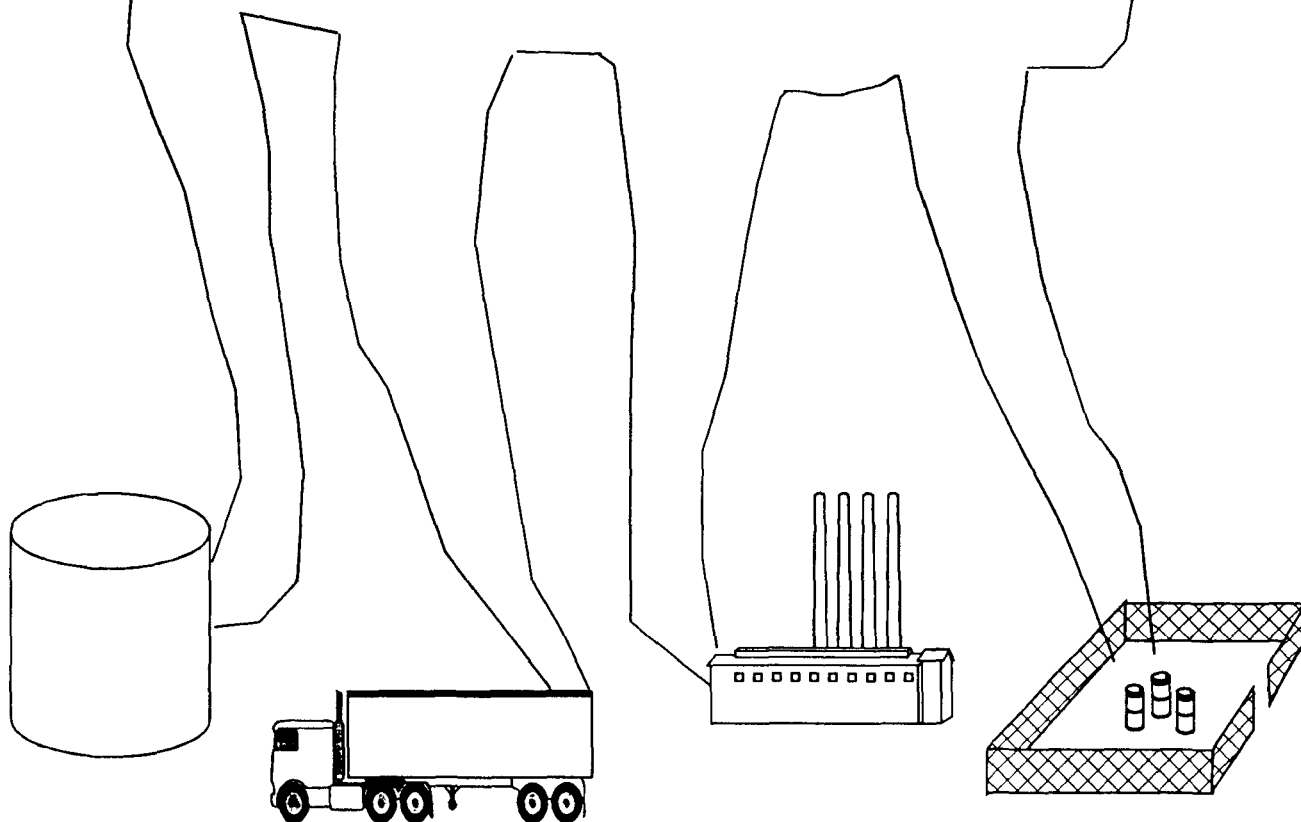
Thermo Environmental Instruments

Thermo Environmental Instruments manufactures the Model 511 Portable Gas Chromatograph. The main features of this GC is the variety of available detectors (FID, PID, ECD, TCD) and their easy changeability. The unit does not have a built-in data handler, so an external integrator or microprocessor is needed.

SUMMARY

Gas chromatography is a separation technique that can be used for identification of the components of a mixture. Portable GCs can be used in the field for a variety of applications. This process of identification can be affected by many factors that must be considered to ensure quality of data. Because the equipment is more complicated to operate than most direct-reading instruments, operators require more training and experience.

AIR DISPERSION MODELING DURING EMERGENCY RESPONSE



Dispersion Modeling During Emergency Response

- Objectives:**
- List five major atmospheric dispersion considerations
 - Describe the concept of stability as it applies to air modeling
 - Given a set of environmental conditions, choose the relevant stability class

Dispersion Modeling During Emergency Response

- Objectives:**
- Describe the concept of Gaussian plume distribution
 - Define near-field meandering and its effects to onsite receptors
 - Given an air dispersion model, list the data inputs needed to run the model for an emergency response
 - Given an emergency response scenario, list the elements of the modeling plan

Notes:

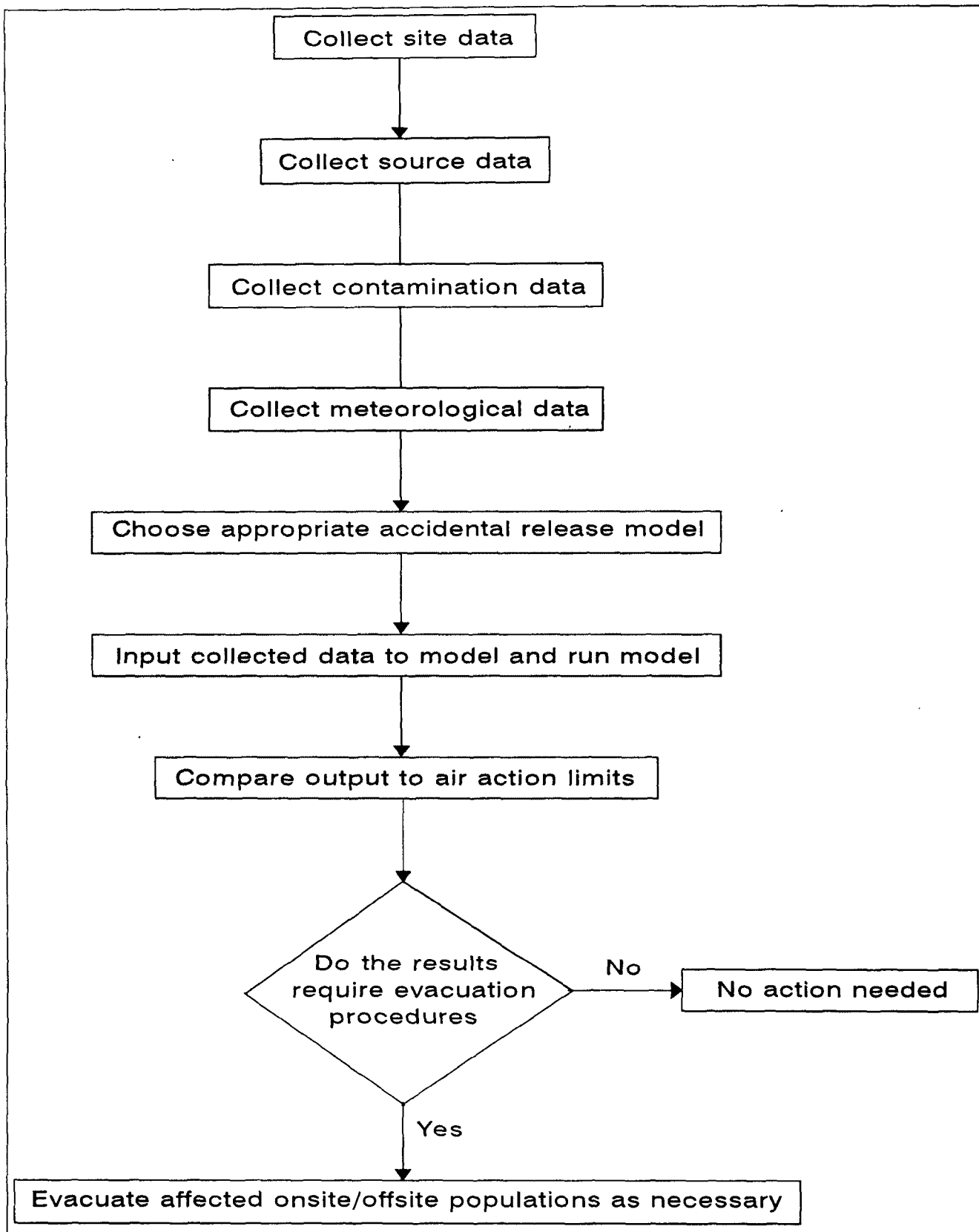


Figure 1. Dispersion modeling during emergency removal.

Dispersion Model Classes	
<p>Physical Models</p> <p>Small-scale, laboratory representations of the overall process (e.g., wind tunnel, water tank)</p>	<p>Mathematical Models</p> <p>A set of analytical or mathematical algorithms that describe the physical and chemical aspects of the problem (e.g., ALOHA, ISC, and PAL)</p>

Dispersion Model Classes

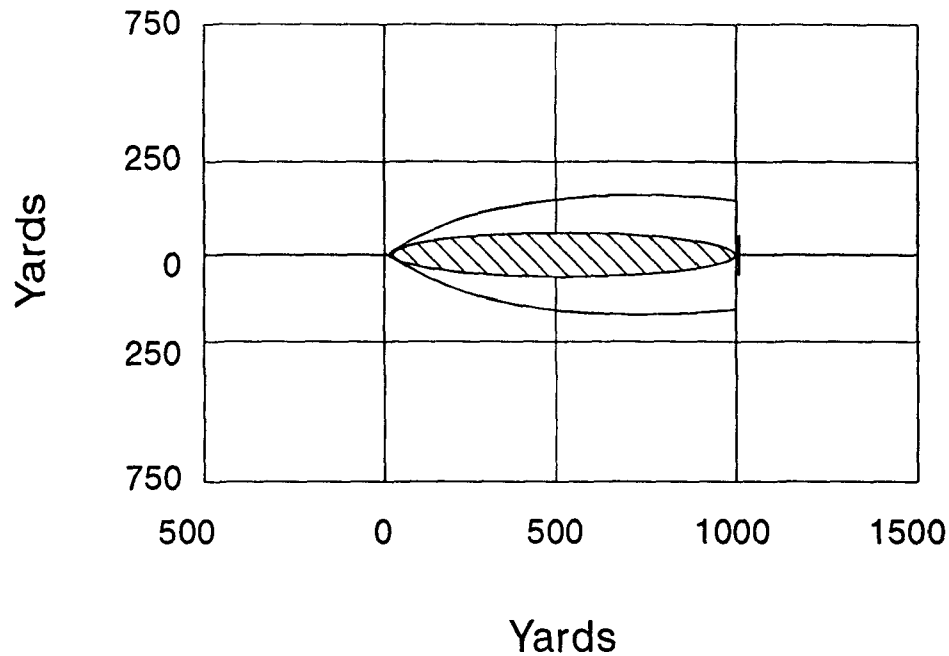
Mathematical models are primarily used because physical models (especially in an emergency response) are much less practical for most Superfund applications.

Mathematical models can be:

- Deterministic models, based on fundamental mathematical descriptions of atmosphere processes, in which effects (i.e., air pollution) are generated by causes (i.e., emissions).
- Statistical models, based on semi-empirical statistical relationships among available data and measurements.

Notes:

Diffusion Model Footprint



Reproduced with permission from The National Safety Council

Diffusion Model

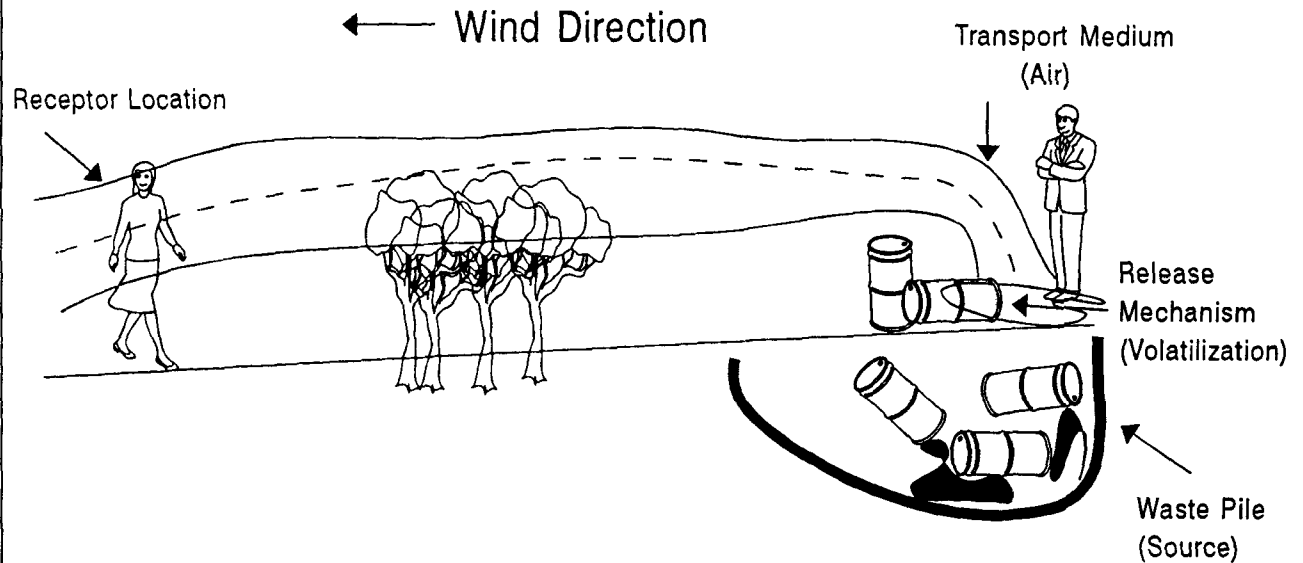
An example of a deterministic model is a diffusion model from which the output (the concentration field or footprint) is computed from mathematical manipulations of specified inputs (emission rates and atmospheric parameters).

A statistical model is given by the forecast, in a certain region, of the concentration levels in the next few hours as a statistical function of:

1. The current available measurements
2. The past correlation between these measurements and the concentration trends.

Notes:

Source-Receptor Relationship



Source-Receptor Relationship

The source-receptor relationship is the goal of studies aimed either at improving ambient air quality (usually the Superfund site goal) or preserving the existing concentration levels from future urban and industrial development. Only a deterministic model can provide an unambiguous assessment of the fraction of the responsibility of each pollutant source to each receptor area. This information then allows the definition and implementation of appropriate emission control strategies.

Notes:

Dispersion Modeling Applications

The two major dispersion modeling applications for Superfund are:

- To design an air monitoring program
- To estimate concentrations at receptors of interest

Dispersion Modeling Applications

Dispersion models can be used when designing an air monitoring program to see how offsite areas of high concentration relate to actual receptor locations. Places where high concentration areas correspond to actual receptors are priority locations for air monitoring stations.

Dispersion models can also be used to provide seasonal dispersion concentration patterns based on available representative historical meteorological data (either onsite or offsite). These dispersion patterns can be used to evaluate the representativeness of any air monitoring data collection period. Data representativeness is determined by comparing the dispersion concentration patterns for the air monitoring period with historical seasonal dispersion concentration patterns.

It is often not practical to place air monitoring stations at actual offsite receptor locations of interest. It will be necessary, however, to characterize concentrations at these locations to conduct a health and environmental assessment. In these cases, dispersion patterns based on modeling results can be used to extrapolate concentrations monitored at the site to offsite receptor locations.

Notes:

Atmospheric Dispersion Considerations

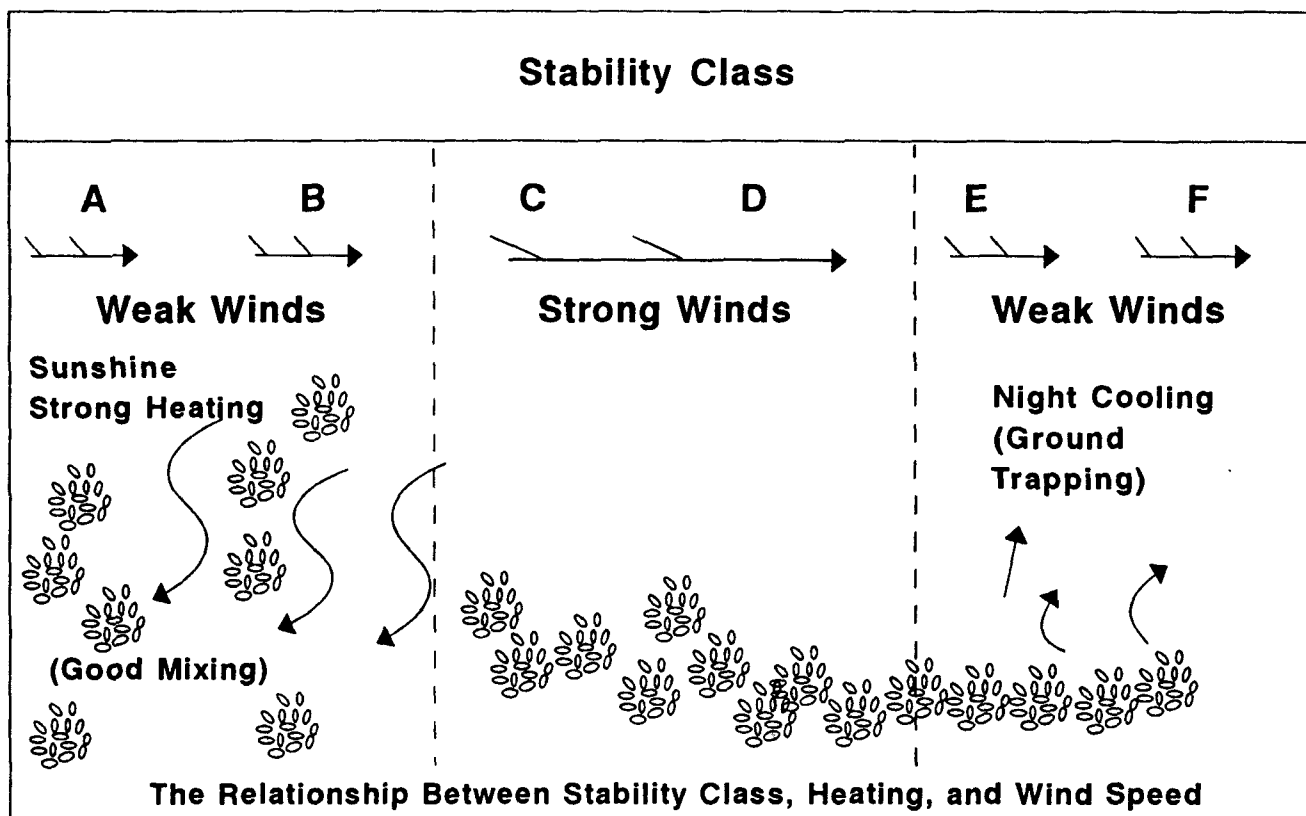
- Stability
- Inversions
- Wind speed and direction
- Air temperature
- Terrain effects

Atmospheric Dispersion Considerations

There are many different types of dispersion models, ranging from simple models that only require a few basic calculations to three-dimensional models that require massive amounts of input data and intense computational platforms to handle the complexity. Choosing the model to use depends on the scale of the problem, the level of detail available for input, the required output, the background of the user, and the turnaround time needed for an answer.

The five atmospheric dispersion considerations (i.e., stability, inversions, wind speed and direction, air temperature, and terrain effects) must all be considered throughout the modeling process.

Notes:

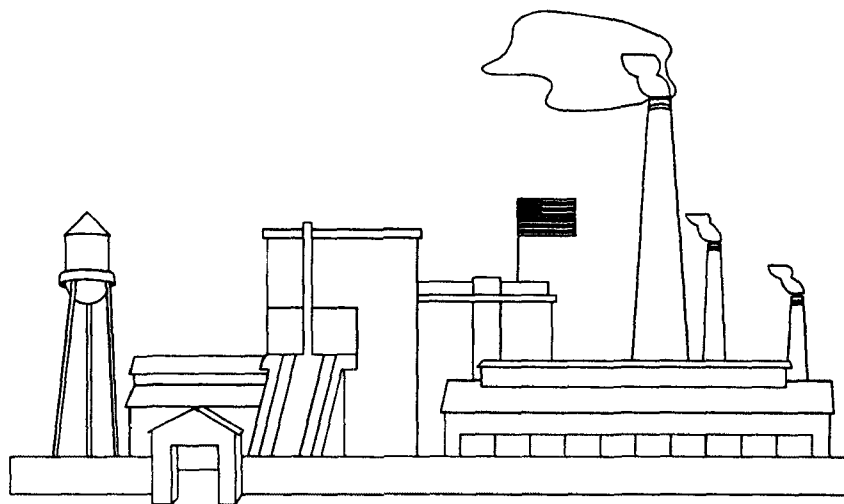


Stability Class

Atmospheric stability is the extent of physical stirring and mixing on the vertical plane. When an atmosphere is stable, there will be little mixing, which results in a persistent concentration. Stable conditions will also generally result in longer, narrower plume shapes.

Notes:

Inversions

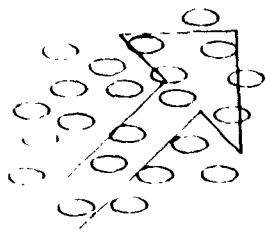


Inversions

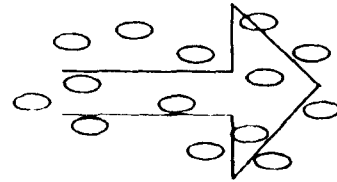
Inversions limit upward movement of air masses due to temperature differentials. The inversion height a modeler is concerned with is generally less than 100 feet. Inversions are generally an evening/night-time phenomenon and their presence results in increased stability.

Notes:

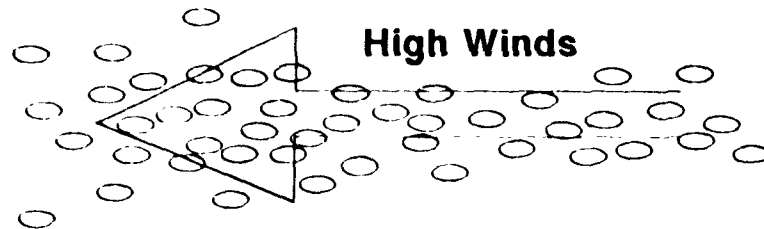
Effects of Wind Speed and Direction



Weak Winds



Moderate Winds



High Winds

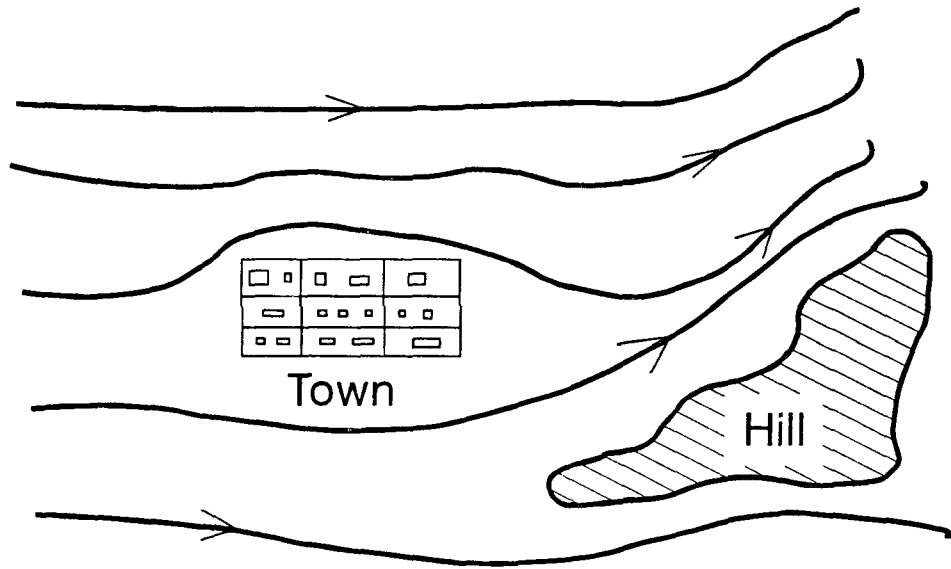
Effect of Wind Speed and Direction on a Plume

Effects of Wind Speed and Direction

Weak winds result in a decrease in stability. As wind speed increases, a corresponding increase in atmospheric stability is produced.

Notes:

Ground Roughness - Terrain Steering Effects

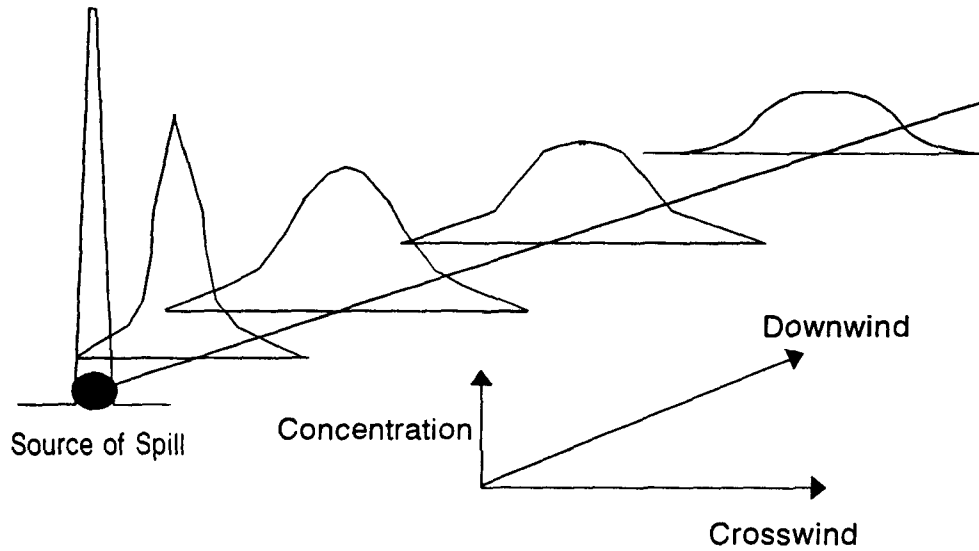


Ground Roughness - Terrain Steering Effects

Areas with hills or valleys may experience wind shifts where the wind actually flows between hills or down into the valleys, turning where these features turn.

Notes:

Gaussian Dispersion

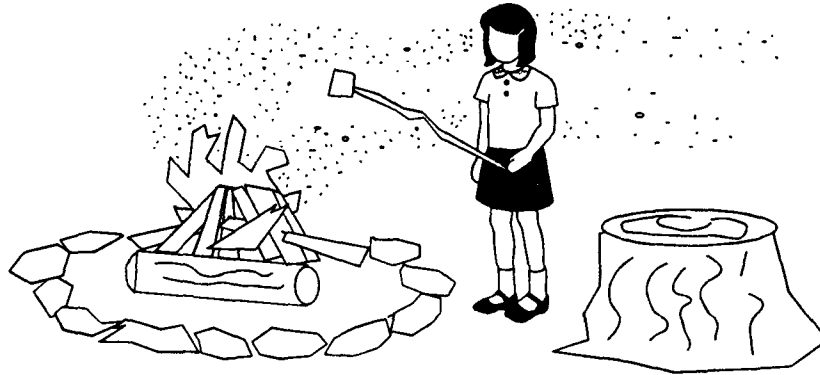


Gaussian Dispersion

In a Gaussian dispersion model, a curve is used to describe how a contaminant will be dispersed in the air after it leaves the source. At the source, the concentration of the contaminant is very high and the Gaussian distribution looks like a spike or a tall column. As the contaminant drifts farther downwind, it spreads out and the "bell shape" gets continually wider and flatter.

Notes:

Near-Field Meandering



Near-Field Meandering

Near-field meandering is caused by individual drifting eddies in the wind that push the plume from side to side. These eddies, or small gusts, are also responsible for much of the mixing that makes the plume spread out. As the plume drifts downward from the spill source, these eddies shift and spread the plume until it takes on the form of a Gaussian distribution.

Notes:

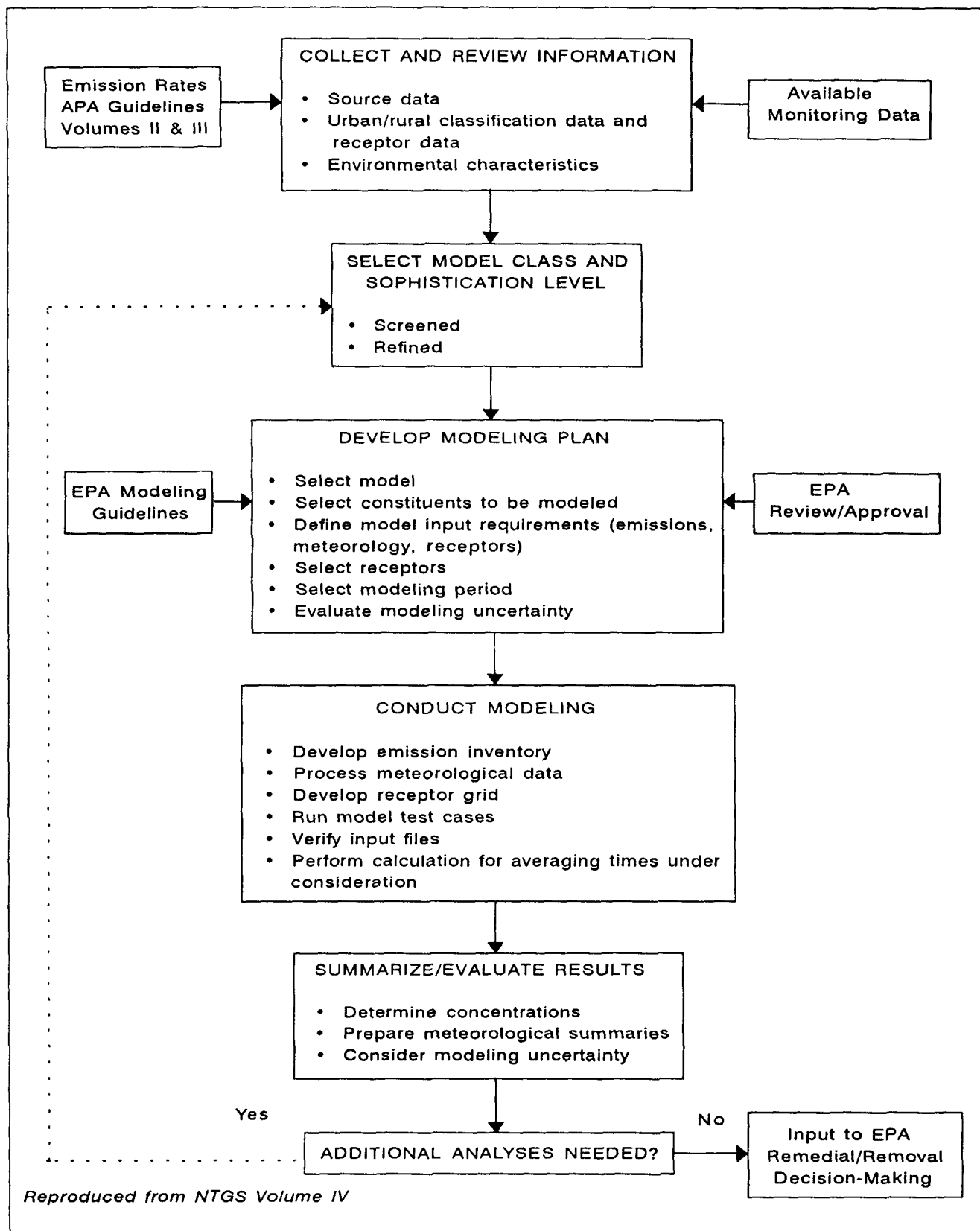


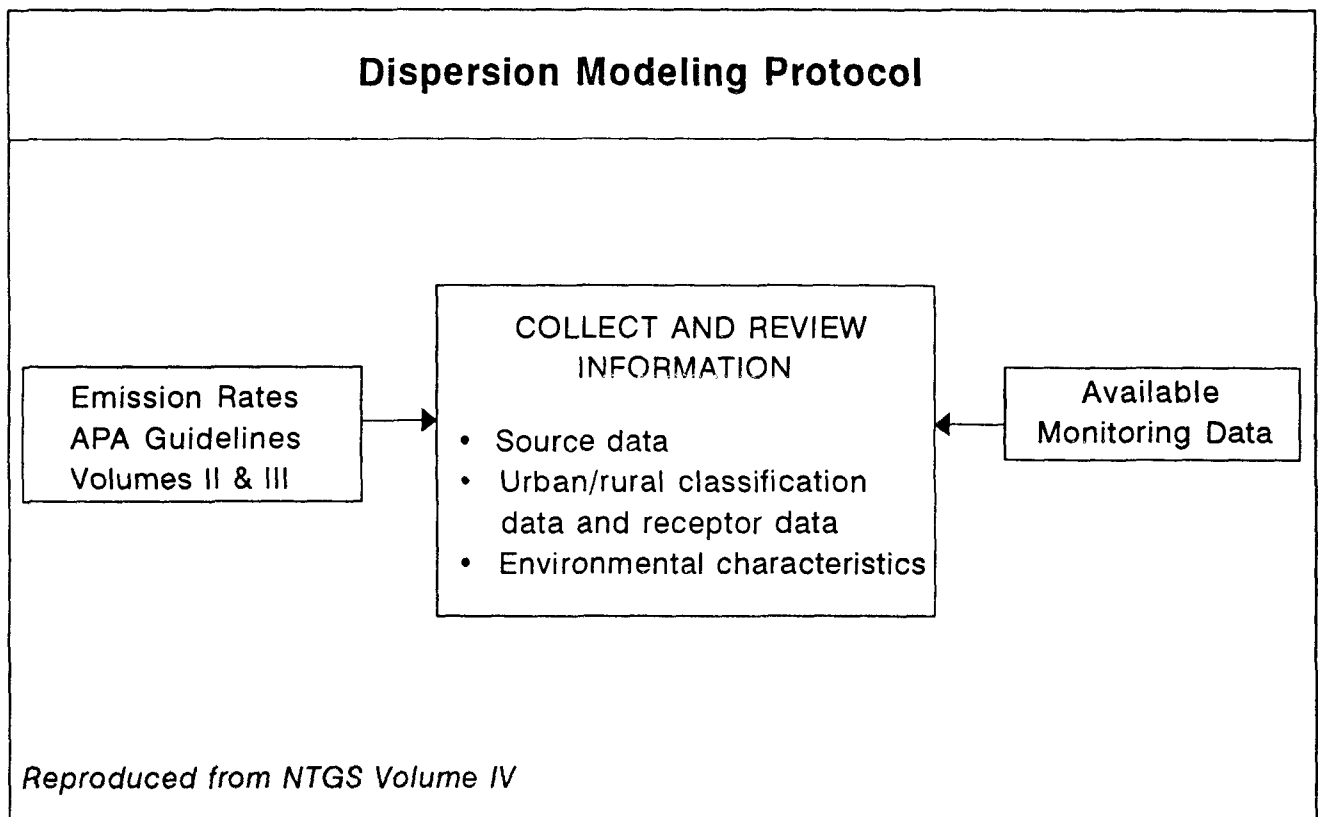
Figure 2. Superfund air impact assessment dispersion modeling protocol.

Superfund Air Impact Assessment Dispersion Modeling Protocol

Associated guidance documents:

- National Technical Guidance Study (NTGS) Volumes II and III
- Air quality modeling at Superfund sites factsheet
- Guidelines on air quality models (revised).

Notes:



Step 1:

Step 1 involves collecting and compiling existing information pertinent to air dispersion modeling. This information is obtained during a literature survey. Information that should be collected and compiled includes source data, receptor data, and environmental data (e.g., land use classification, demography, topography, and meteorology). Once the existing data have been collected and compiled, a thorough evaluation will define the data gaps. A coherent dispersion modeling plan can then be developed using site-specific parameters and requirements.

Notes:

Dispersion Modeling Protocol

SELECT MODEL CLASS AND SOPHISTICATION LEVEL

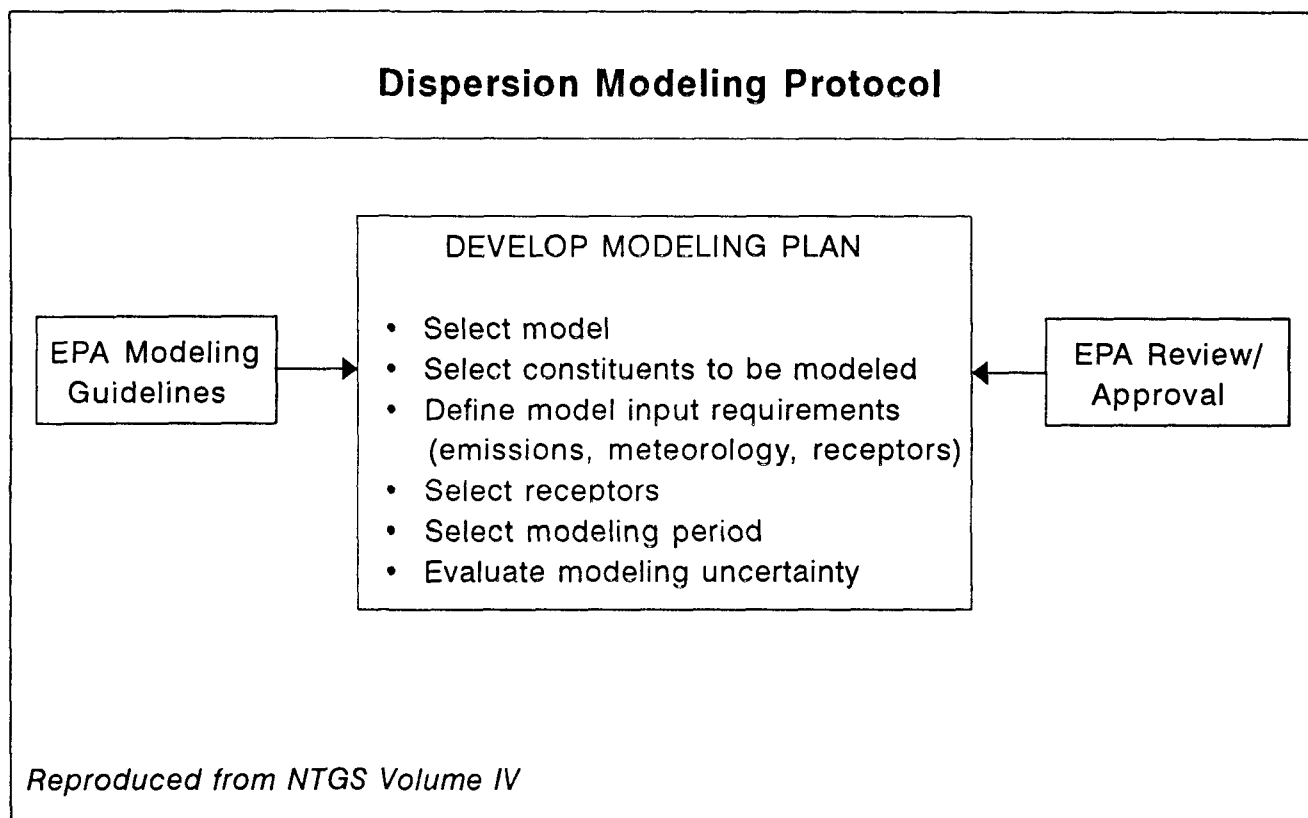
- Screened
- Refined

Reproduced from NTGS Volume IV

Step 2:

Step 2 involves the selection of the dispersion modeling sophistication level and screening and refined modeling techniques. The selection process depends on program objectives as well as available resource and technical constraints. Screening models generally use limited and simplified input information to produce a conservative estimate of exposure. Screening models assist in the initial determination of whether the Superfund site, or site activity, will present an air impact problem. The emission source(s) should then be evaluated with either a more sophisticated screening technique or a refined model. When selecting a more sophisticated modeling technique or approach, the following aspects should be considered: availability of appropriate modeling techniques for the Superfund list of toxic constituents; site-specific factors, including source configuration and characteristics; applicability; limitations; performance for similar applications; and comparison of advantages and disadvantages of alternative modeling techniques and approaches.

Notes:



Step 3:

Step 3 involves preparing a dispersion modeling plan. Elements that should be addressed in the plan include overview of the Superfund site area, selection of constituents to be modeled, modeling methodology (emission inventory, meteorology, receptor grid, rural/urban classification, models to be used, concentration averaging time, and special situations such as wake effects), and documentation of the air modeling plan.

Notes:

Dispersion Modeling Protocol

CONDUCT MODELING

- Develop emission inventory
- Process meteorological data
- Develop receptor grid
- Run model test cases
- Verify input files
- Perform calculation for averaging times under consideration

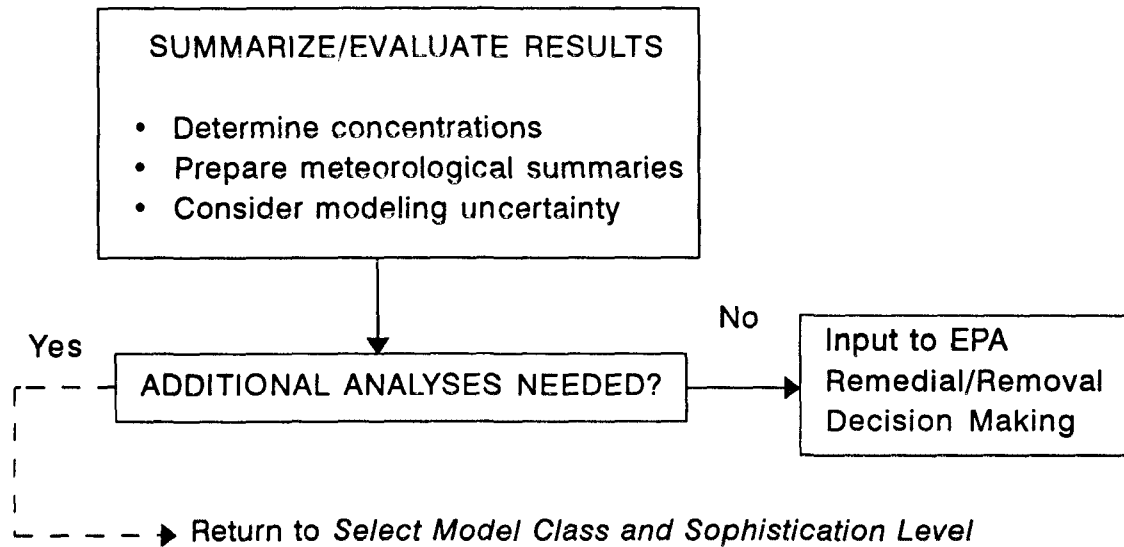
Reproduced from NTGS Volume IV

Step 4:

Step 4 specifies the actual activities involved in conducting air dispersion modeling for a Superfund site. Activities that are performed include developing an emission inventory, preprocessing and verifying modeling, setting model switches, running model test cases, performing dispersion calculations, and obtaining a printout of modeling input and output.

Notes:

Dispersion Modeling Protocol



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Step 5:

Step 5 involves the review and assessment of the dispersion modeling results.

Additional components of this step include preparation of data summaries, concentration mapping (i.e., isopleths), estimation of uncertainties, and assessment.

Notes:

Accidental Release Modeling

- Provides worst-case results
- Results used to determine evacuation of shelter-in-place options
- Cannot account for near-field patchiness
- Examples: ALOHA[™], ARCHIE, CHARM[™], TRACE, and TSCREEN

Accidental Release Modeling

Accidental release modeling is performed when results are needed immediately. Accidental release models that assist in making source-term calculations, or provide probability warnings, are best when real-time solutions are essential.

ALOHA[™], ARCHIE, CHARM[™], TRACE, and TSCREEN are examples of accidental release models.

Each model is a relatively simple estimation technique that provides conservative estimates of air quality impact(s).

Notes:

Accidental Release Models

ALOHA™ (NOAA/EPA)

Areal

Locations

Of

Hazardous

Atmospheres

ALOHA™

The Areal Locations of Hazardous Atmospheres (ALOHA) model was developed through a joint venture between the National Oceanic and Atmospheric Administration (NOAA) and EPA. It is an emission estimation and air quality dispersion model for estimating the emission rate, movement, and dispersion of gases released into the atmosphere. The model estimates pollutant concentrations downwind from the source of a release, taking into account the toxicological and physical characteristics of the material. ALOHA considers the physical characteristics of the release site, the atmospheric conditions, and the initial source conditions.

The model has a built-in database of chemical names and properties that the model uses to calculate emission rates. The program performs buoyant gas dispersion based on Gaussian dispersion equations and heavier-than-air dispersion based on algorithms in the DENSE GAS DISPERSION (DEGADIS) model.

Emission estimations can be made for puddles, tanks, and pipe releases or for direct input of material into the atmosphere. The model uses hourly meteorological data that can be entered by the user or obtained from real-time measurements. The results of the model can be displayed as concentration plots or in text summary screens. The concentration outputs are limited to a 1-hour (or less) exposure.

Notes:

Accidental Release Models

ARCHIE (FEMA/DOT/EPA)

Automated

Resource for

Chemical

Hazard

Incident

Evaluation

ARCHIE

The Automated Resource for Chemical Hazard Incident Evaluation (ARCHIE) model was developed through a joint effort by the Federal Emergency Management Agency (FEMA), the U.S. Department of Transportation (DOT), and EPA. It is an emission estimation and atmospheric dispersion model that can be used to assess the vapor dispersion, fire, and explosion impacts associated with episodic discharges of hazardous materials into the environment. The model can estimate the emissions and duration of liquid/gas releases from tanks, pipelines, and liquid pools, as well as the associated ambient concentrations downwind of these releases. ARCHIE can also evaluate the thermal hazards resulting from the ignition of a flammable release and the consequences of an explosion caused by a flammable gas, tank overpressurization, or ignition of an explosive material. In addition, it can estimate the size of the downwind hazard zone that may require evacuation or other public protection because of the release of a toxic gas or vapor into the atmosphere.

To estimate downwind concentrations, simulated meteorological conditions are input to the model. The user must input chemical properties of the material released from information contained in the material safety data sheets.

Notes:

Accidental Release Models

CHARMTM (Radian Corporation))

Complex

HAzardous

Release

Model

CHARMTM

The Complex Hazardous Release Model (CHARMTM) is a proprietary Gaussian puff model for continuous and instantaneous releases of gases or liquids. The model is configured to handle chemicals that are buoyant, neutrally buoyant, or heavier-than-air. CHARMTM can estimate the emission rates of chemicals using a modification of the SHELL spill model and a multiphase pressurized gas release model. CHARMTM contains a database of chemical information that is used in calculating emission estimates. The program is menu driven and can accept simulated meteorological data for up to 24 hours. The CHARMTM model can simulate the transport of chemicals in spatially and temporally varying wind fields. The results from the program may be displayed graphically on a screen or output to a printer.

Notes:

Accidental Release Models

TRACE (E.I. Dupont de Nemours)

Toxic

Release

Analysis of

Chemical

Emissions

TRACE

The SAFER System TRACE model is an engineering analysis tool for dispersion modeling. It models accidental toxic releases, including those caused by pipe/flange leaks, aqueous spills, hydrogen fluoride spills, fuming acid spills, stack emissions, or elevated dense gas emissions. The program is menu driven and contains several modules to estimate the evaporation and dispersion of chemicals and analyze the effect of certain parameters on downwind concentrations. The program has a built-in database of chemicals and their properties and various source-term modules. The model uses real-time or simulated meteorological data for atmospheric dispersion calculations. These data can vary with time during the release. The results of the modeling analysis can be displayed visually on graphs or stored in tables.

Notes:

Accidental Release Models

TSCREEN (EPA)

- Model for screening toxic air pollutant concentrations

TSCREEN

TSCREEN, a model for screening toxic air pollutant concentrations, is an air quality dispersion model that implements the procedures in *A Workbook of Screening Techniques for Assessing Impacts of Toxic Air Pollutants* (EPA-450-88-009). The TSCREEN model is an atmospheric dispersion model that uses the dispersion algorithms of SCREEN, Release Valve Discharge (RVD), and PUFF models. It automatically selects the worst-case simulated meteorological conditions based on the criteria presented in the workbook. The model contains a data table of chemicals and their associated parameters (limited to two chemicals at this time) that TSCREEN can access. It can calculate the source term for dust particles within a pile of a specified dimension. The model can also simulate the dispersion of gaseous, liquid, and particulate matter releases. TSCREEN outputs graphical and tabular summaries of predicted pollutant concentrations.

Notes:

ACCIDENTAL RELEASE MODELS

CRITERIA	ALOHA ⁽¹⁾	ARCHIE	CHARM	DEGADIS	PUFF*	TSCREEN	TRACE ⁽¹⁾
Model Capabilities User friendliness	X	X	X			X	X
Hardware/Equipment	DOS/MAC	DOS	DOS	DOS	DOS	DOS	DOS
Emission Source Information Constant/variable emission Spills Tank/pipe leaks Fire/explosions Stack/vents Buoyant/dense gas/liquid	X X X X	X X X X	X	X X X X	 X	 X X	X X X X
Atmospheric Dispersion Gaussian dispersion Buoyant dispersion Dense gas	X X X	X X	X X	X X	X X	X X X	X X X
Real-Time Computations	X	X	X			X	X
Averaging Periods	V		1-24 HOURS		V	1 HOUR	SS
Data Output Store to file Display on screen Graphic output	X X X	X	X X X	X	X X X	X X X	X X X
Meteorological Data Historical Real-time/onsite Simulated/worst-case	 X X	 X	X X	 X	 X	 X	 X X
Chemical Database	X		X			L	X

V = Variable (computer generated)

SS = Several (by selection)

L = Limited

⁽¹⁾ = Models most often used

* = Model using the PUFF algorithm.

Source: Air Quality Modeling at Superfund Sites factsheet.

Notes:

REFERENCES

The following list represents a partial list of background references on the subject of air monitoring and sampling. Although other sources may be available, it is believed that these will provide the reader with a good understanding of the subject.

The references are listed alphabetically by title and include author, publisher, and place of publication. The year of publication is given for governmental sources only. For the remainder, the reader should attempt to obtain the most recent edition. An * after the title indicates that a copy of the document is part of the course library and is available for review.

1. *Advances in Air Sampling**
Lewis Publishers, Inc.
121 South Main Street
P.O. Drawer 519
Chelsea, MI 48118
(Also available through ACGIH. See #4.)
2. Air Methods Database
Available on the Cleanup Information electronic bulletin board (CLU-IN), formerly OSWER BBS. For further information, call 301 589-8366.
3. *Air Monitoring For Toxic Exposures: An Integrated Approach**, 1991
Shirley A. Ness
Van Nostrand Reinhold
115 Fifth Avenue
New York, NY 10003
4. *Air Monitoring Instrumentation: A Manual for Emergency, Investigatory, and Remedial Responders**, 1993
C. Maslonsky and S. Maslonsky
Van Nostrand Reinhold
115 Fifth Avenue
New York, NY 10003
5. *Air Sampling Instruments**
American Conference of Governmental Industrial Hygienists
6500 Glenway Avenue, Building D-E
Cincinnati, OH 45211
513 661-7881
6. Air/Superfund National Technical Guidance Series:
 - *Volume IV—Guidance for Ambient Air Monitoring at Superfund Sites (revised)*. EPA-451/R-93-007, May 1993

- *Compilation of Information on Real-Time Air Monitoring for Use at Superfund Sites.*
EPA-451/R-93-008, May 1993
7. *Atmospheric Analysis: Occupational Health and Safety*, ASTM Standards, Volume 11.03
American Society for Testing and Materials
1916 Race Street
Philadelphia, PA 19103-1187
215 299-5400
 8. *Basic Gas Chromatography*
H.M. McNair and E.J. Bonelli
Varian Instrument Division
Purchase from Supelco, Inc.
Supelco Park
Bellefonte, PA 16823-0048
 9. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*,
EPA/600/4-89/017, June 1988
Atmospheric Research and Exposure Assessment Laboratory
U.S. Environmental Protection Agency
Office of Research and Development
Research Triangle Park, NC 27711
 10. *A Compendium of Superfund Field Operations Methods**, EPA/540/P-87/001, December 1987
U.S. Environmental Protection Agency
Office of Emergency and Remedial Response
Office of Waste Programs Enforcement
Washington, DC 20460
 11. *Data Quality Objectives for Remedial Response Activities: Development Process*,
EPA/540/G-87/003, March 1987
U.S. Environmental Protection Agency
Office of Emergency and Remedial Response
Office of Waste Programs Enforcement
Washington, DC 20460
 12. *Fundamentals of Industrial Hygiene*
National Safety Council
444 North Michigan Avenue
Chicago, IL 60611
 13. *Guidance on Applying the Data Quality Objectives Process for Ambient Air Monitoring
Around Superfund Sites (Stages I & II)*, EPA-450/4-89-015; *(Stage III)*, EPA-450/4/90-005
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

14. *Guide to Occupational Exposure Values**
American Conference of Governmental Hygienists
6500 Glenway Avenue, Building D-E
Cincinnati, OH 45211
513 661-7881
15. *Guide to Portable Instruments for Assessing Airborne Pollutants Arising from Hazardous Wastes*
International Organization of Legal Metrology
Paris, France
(Available through ACGIH)
16. *The Industrial Environmental - Its Evaluation and Control, 1973*
National Institute for Occupational Safety and Health
Rockville, MD
(Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402 [202 783-3238])
17. *Industrial Hygiene and Toxicology, Volumes I and III*
Frank A. Patty
John Wiley and Sons, Inc.
New York, NY
18. *Manual of Recommendation Practice for Combustible Gas Indicators and Portable Direct Reading Hydrocarbon Detectors, 1980, 1st edition*
John Klinsky (ed)
American Industrial Hygiene Association
Akron, OH
19. *Methods of Air Sampling and Analysis**
Lewis Publishers, Inc.
121 South Main Street
P.O. Drawer 519
Chelsea, MI 48118
(Also available through ACGIH)
20. *NIOSH Manual of Analytical Methods, Editions 1, 2, and 3**
National Institute for Occupational Safety and Health
Rockville, MD
(Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402 [202 783-3238])
21. *OSHA Analytical Methods Manual**
Superintendent of Documents
U.S. Government Printing Office
Washington, DC 20402
202 783-3238

22. *OSHA Technical Manual*^{*}, 1990
(See ACGIH)
23. *Removal Program Representative Sampling Guidance: Air*
U.S. Environmental Protection Agency
Office of Emergency and Remedial Response
Emergency Response Division
Environmental Response Branch
Washington, DC
24. *Standard Operating Safety Guides*, June 1992
U.S. Environmental Protection Agency
Environmental Response Team
2890 Woodbridge Avenue
Building 18 (MS-101)
Edison, NJ 08837-3697
908 321-6740
25. *Standard Operating Guide for the Use of Air Monitoring Equipment for Emergency Response*
(See #21)
26. *Standard Operating Guide for Air Sampling and Monitoring at Emergency Responses*
(See #21)
27. *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, EPA-600/4-83-027
U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Research Triangle Park, NC 27711

MANUFACTURERS AND SUPPLIERS OF AIR MONITORING EQUIPMENT

AIR MONITORING EQUIPMENT

Aerosol/Particulate Direct-Reading Monitors:

- Air Techniques Incorporated
- HUND Corporation
- Met One, Inc.
- MIE, Inc.
- MST Measurement Systems, Inc.
- Pacific Scientific (HIAC/ROYCO Instrument Division)
- Particle Measuring Systems, Inc.
- PPM Enterprises
- TSI Incorporated

Calibration Gases: (most manufacturers of instruments provide calibration gases for use with their instruments; these companies provide a variety of calibration gases)

- Airco Industrial Gases
- Alphagaz
- Bryne Specialty Gases
- Digicolor
- Environics, Inc.
- GC Industries
- Kin-Tek laboratories, Inc.
- Liquid Air Corporation
- National Specialty Gases
- Norco, Inc.
- Scott Specialty Gases
- VICI Metronics

Calibrators, Pump:

- Accura Flow Products Co., Inc.
- Air Systems International
- AMETEK
- BGI Incorporated
- BIOS International Corp
- DuPont
- Gillian Instrument Co.
- Sensidyne

- SKC, Inc.
- Spectrex Corporation

Canister Samplers:

- Andersen Samplers Incorporated
- Nutech Corporation
- Scientific Instrumentation Specialists
- Wedding & Associates, Inc.
- Xontech, Inc.

Collection Media:

- Ace Glass Incorporated
- BGI Incorporated
- DACO Products
- Gelman Sciences
- Gilian Instrument Corporation
- Hi-Q Environmental Products Company
- LaMotte Chemical Products Company
- Micro Filtration Systems
- Millipore Corporation
- Mine Safety Appliances Company
- Nuclepore Corporation
- Omega Specialty Instruments Company
- Paliflex, Inc.
- Poretics Corporation
- Schleicher & Schuell
- Sipin, Anatole, J., Co., Inc.
- SKC, Inc.
- Supelco, Inc.

Colorimetric Detectors: (B = badges or dosimeters; DT = regular detector tubes; LT = long term detector tubes)

- American Gas & Chemical Co., Ltd. (B)
- Analytical Accessories International (B)
- Bacharach, Inc. (B)
- Chemsense (B)
- Crystal Diagnostics (B)
- Enmet Corporation (DT, LT)
- GMD Systems, Inc. (B)
- Matheson Safety Products (DT, LT)
- MDA Scientific (B)
- Mine Safety Appliances Co. (B, DT, LT)

- National Draeger, Inc. (B, DT, LT)
- PPM Enterprises (B)
- Sensidyne (DT), Inc.
- SKC, Inc. (B, LT)
- VICI Metronics (B)
- Willson Safety Products (B)

Combustible Gas Meters:

- A.I.M. Safety Company, Inc.
- Astro International Corp.
- Bacharach Instruments
- Biosystems, Inc.
- Chestec, Inc.
- Control Instruments Corp.
- Dynamation Incorporated
- Energy Efficiency Systems, Inc.
- Enmet Corporation
- GasTech, Inc.
- GfG America Gas Detection Ltd.
- Grace Industries, Inc.
- Heath Consultants Incorporated
- Industrial Scientific Corporation
- J and N Enterprises, Inc.
- Lumidor Safety Products e.s.p., Inc.
- Mine Safety Appliances Co.
- National Draeger, Inc.
- Neotronics N.A., Inc.
- Quatrosense Environmental Ltd.
- Scott Aviation
- Sieger Gas Detection
- Sierra Monitor Corporation
- Texas Analytical Controls, Inc.
- TIF Instruments, Inc.

Gas Bags:

- AeroVironment, Inc.
- The Anspec Company, Inc.
- BGI Incorporated
- Calibrated Instruments, Inc.
- Digicolor
- Jensen Inert
- KVA Analytical Systems
- Norton Performance Plastics
- Nutech Corporation

- Plastic Film Enterprises
- Pollution Measurement Corporation
- Science Pump Corporation
- SKC, Inc.

Gas Chromatographs: (types of detectors available: AID = argon ionization; ECD = electron capture; FID = flame ionization; MS = mass spectroscopy; PID = photoionization; SS = chemical specific sensor; TCD = thermal conductivity)

- Bruker Instruments (MS)
- Canaan Scientific Products
- CMS Research Corporation (SS)
- The Foxboro Company (FID)
- GOW-MAC (FID, TCD)
- HNU Systems, Inc. (PID, FID)
- Microsensor Systems Inc.
- Microsensor Technology, Inc. (TCD)
- Photovac Incorporated (PID, FID)
- S-Cubed (ECD)
- Sensidyne (FID)
- Sentex Sensing Technology, Inc. (ECD, PID, PID, TCD)
- Summit Interests (FID, PID, TCD)
- Thermo Environmental Instruments, Inc. (ECD, FID, PID, TCD)
- Viking Instruments (MS)
- XonTech, Inc. (AID, ECD)

Oxygen Meters:

- A.I.M. Safety Company, Inc.
- Bacharach, Inc.
- Biosystems, Inc.
- Dynamation Incorporated
- Energy Efficiency Systems, Inc.
- Enmet Corporation
- GasTech, Inc.
- GC Industries
- GfG America Gas Detection Ltd.
- Industrial Scientific Corporation
- Lumidor Safety Products e.s.p., Inc.
- MDA Scientific, Inc.
- Metrosonics, Inc.
- Mine Safety Appliances Co.
- National Draeger, Inc.
- Neotronics N.A., Inc.
- Rexnord Safety Products
- Scott Aviation

- Sensidyne
- Sieger Gas Detection
- Sierra Monitor Corporation
- Teledyne Analytical Instruments

Passive Dosimeters: (these devices require laboratory analysis; for direct-reading dosimeters see G. Colorimetric Detections)

- Advanced Chemical Sensors
- Air Technology Labs, Inc.
- Assay Technology
- EnSys, Inc.
- Gilian Instrument Corporation
- Landauer, R.S. Jr. & Company
- Mine Safety Appliances Co.
- National Draeger, Inc.
- Pro-Tek Systems, Inc.
- Sensidyne
- SKC, Inc.
- 3M

Sampling Pumps and Accessories: (letters denote primary function of pumps and apparatus: P = Personal; A = Area; B = Bag filling)

- AeroVironment, Inc. (B)
- Air Systems International, Inc. (A)
- AMETEK (P)
- Analytical Accessories International (A,P)
- Andersen Samplers Incorporated (A)
- Arjay Equipment Corporation (A)
- Barnant Company (A)
- BGI Incorporated (P, A)
- BIOS International Corp
- Calibrated Instruments, Inc. (B)
- California Measurements, Inc. (A)
- DuPont (P)
- Environmetrics, Inc. (A)
- General Metal Works, Inc. (A)
- Gillian Instrument Corp. (P)
- LaMotte Chemical Products Company (A)
- Midwest Environics, Inc. (A)
- Mine Safety Appliances Co. (P)
- Omega Specialty Instrument Co. (A)
- Wedding & Associates, Inc. (A)
- Sensidyne (P)
- Sipin, Anatole J., Co., Inc. (P)

- SKC, Inc. (P)
- Spectrex Corporation (P)
- Staplex Air Sampler Division (A)
- Supelco, Inc. (P)
- Thermedics, Inc. (P)
- Wedding & Associates (A)

Toxic Monitors: (direct-reading instruments for low concentrations of contaminants; letters denote types of detectors available; PID = photoionization; FID = flame ionization; IR = infrared spectroscopy; TCD = thermal conductivity; GS = general sensor, e.g., MOS or super-sensitive CGI; SS = sensor for specific chemical, e.g., CO, H₂S)

- A.I.M. Safety Company, Inc. (GS, SS)
- Anacon Detection Technology (SS)
- Analect Instruments (IR)
- Arizona Instrument, Jerome Division (SS)
- Astro International Corp. (SS)
- Bacharach, Inc. (GS, SS)
- Biosystems, Inc. (SS)
- Bruel & Kjaer (IR)
- CEA Instruments, Inc. (GS, SS)
- Dynamation Incorporated (GS, SS)
- Enmet Corporation (SS)
- Environmental Technologies Group (GS)
- The Foxboro Company (FID, IR)
- GasTech, Inc. (GS, SS)
- GfG America Gas Detection Ltd. (SS)
- GMD Systems, Inc. (colorimetric)
- GOW-MAC (TCD)
- Grace Industries, Inc. (GS)
- Graesby Ionics Ltd. (Ion Mobility Spectrometry)
- Heath Consultants Incorporated (FID)
- HNU Systems, Inc. (PID)
- Industrial Scientific Corporation (SS)
- International Gas Detectors, Inc.
- Interscan Corporation (SS)
- J and N Enterprises, Inc. (GS)
- MDA Scientific, Inc. (SS)
- Macurco, Inc. (GS, SS)
- Mast Development Corporation (SS)
- Matheson Safety Products (TCD)
- Metrosonics, Inc. (SS)
- Microsensor Systems, Inc. (SS)
- Mine Safety Appliances Co. (PID, FID, SS)
- National Draeger (SS)
- Neotronics N.A., Inc. (SS)

- Nicolet Instrument Corp. (IR)
- Photovac Incorporated (PID)
- Quatrosense Environmental Ltd. (SS)
- Scott Aviation (SS)
- Sensidyne (SS, FID)
- Sentex Sensing Technology, Inc. (FID)
- Servomax Company (IR)
- Sieger Gas Detection (SS, IR)
- Sierra Monitor Corporation (SS)
- Spectrex Corporation (SS)
- Summit Interests (FID, PID, TCD)
- Tekmar Company (TCD)
- Texas Analytical Controls, Inc. (SS)
- Thermo Environmental Instruments, Inc. (FID, PID, TCD)
- TIF Instruments, Inc. (GS)
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415 977-6506

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919 821-2929

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Santa Ana, CA 92705
714 730-9405

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Suite G111-A
Houston, TX 77092
713 939-1103

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617 868-6200

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Columbus, OH 43209
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313 769-0573

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P.O. Box 979
2308 S. Industrial Highway
Ann Arbor, MI 48106-0979
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1-800-645-7490

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Baltimore, MD 21284-9840
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Watford Herts Wb2 2BW
England
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Miami, FL 33266-0824
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Texas City, TX 77590
409 945-3627

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Galmouth, MA 02541-99811
508 540-0561

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Chestertown, MD 21620
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1-800-344-3100

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Miami, FL 33014
305 625-6511

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3946 S. Mariposa Street
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303 781-4062

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Air Monitoring Division
2212 East 12th Street
Davenport, IA 52803
319 326-1041

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Philadelphia, PA 19125
215 423-3200

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30 Seaview Drive
Secaucus, NJ 07096-1587
215 641-2700

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1-800-535-0606

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919 682-0402

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508 256-5450

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203 929-7761

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303 443-7100

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Deer Park, NY 11729
516 254-4199

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313 399-0450

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Chicago, IL 60680
708 383-7794

Poretics Corporation
151 I Lindbergh Avenue
Livermore, CA 94550-9412
415 373-0500
1-800-922-6090

PPM Enterprises
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Knoxville, TN 37922
615 966-8796

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Middletown, NY 10940
914 344-4711

Quatrosense Environmental Ltd.
5935 Ottawa Street
P.O. Box 749
Richmond, Ontario, Canada KOA 2Z0
613/838-4005

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La Jolla, CA 92038-1620
619/453-0060

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800/245-4024

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P.O. Box 8941
Moscow, ID 83843
208/882-3860

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Camden, NJ 08104
609/963-7700

Scott Aviation
225 Erie Street
Lancaster, NY 14086
716/683-5100

Scott Specialty Gases
Route 161 North
Plumsteadville, PA 18949
215/766-8861

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16333 Bay Vista Dr.
Clearwater, FL 34620
813/530-3602
800/451-9444

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Ridgefield, NJ 07657
201/945-3694

Servomax Company
90 Kerry Place
Norwood, MA 02062
617 769-7710

Sieger Gas Detection
405 Barclay Blvd.
P.O. Box 1405
Lincolnshire, IL 60069-1405
1-800-221-1039

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Milipitas, CA 95035
408 262-6611

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New York, NY 10018
212 695-5706

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1-800-752-8472

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415 365-6567

Staplex Company
Air Sampler Division
777 Fifth Avenue
Brooklyn, NY 11232-1695
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1-800-221-0822

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1-800-543-4461

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470 Wildwood Street
Woburn, MA 01888
617 938-3786

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8 West Forge Parkway
Franklin, MA 02038
508 520-0430

Transducer Research, Inc.
999 Chicago Ave.
Naperville, IL 60540
708 357-0004

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Santa Clara, CA 95051
408 737-0550

Viking Instruments Corp.
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Reston, VA 22091-3406
703 758-9339

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Clifton, NJ 07014
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609 825-1400

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Reading, PA 19603-0622
215 376-6161

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600 National Avenue
Mountain View, CA 94043
415 964-3261

XonTech Inc.
6862 Hayvenhurst Avenue
Van Nuys, CA 91406
818 787-7380

AIR MONITORING FOR HAZARDOUS MATERIALS WORKBOOK

CONTENTS

<u>Exercise</u>		<u>Page</u>
1	Oxygen Monitor, Combustible Gas Indicators, and Specific Chemical Monitors	1
2	Photoionization Detectors - Survey	13
3	Flame Ionization Detectors - Survey	21
4	Gas Chromatography - Organic Vapor Analyzer	29
5	Detector Tubes	39
6	Direct-Reading Aerosol Monitors	53
7	Gas Chromatography - Photoionization Detector	63
8	Sampling Pumps and Collection Media	71
9	Field Exercise	87

EXERCISE 1

Oxygen Monitors, Combustible Gas Indicators, and Specific Chemical Monitors

OBJECTIVE

In this exercise, students will calibrate or check the calibration of a variety of combustible gas indicators (CGIs), combination CGI/O₂ monitors, and combination CGI/O₂/toxic monitors. The instruments will then be used to sample a variety of test atmospheres and the results will be interpreted.

PROCEDURE

The exercise is divided into three different stations. Each station is equipped with an air monitoring instrument or group of instruments.

Station 1: MSA Model 260/261 combination CGI/O₂ monitor

Station 2: MSA Model 360 combination CGI/O₂/carbon monoxide monitor

Station 3: GasTech Model 1314 combination CGI/O₂/toxic monitor

There may be more than one of each numbered station to reduce crowding. Follow the instructions given for each instrument. Sample the indicated gas bags and record your results. At the end of the exercise, answer the questions. The instructor will then hold a brief discussion.

The instructions given for each instrument are based on the manufacturers' operating manuals. However, some steps may have been added for illustration purposes and some may have been shortened for purposes of time or space. As with any instrument, consult the operator's manual before using in the field.

STATION 1

MSA Model 260/261 Combination CGI/O₂ Monitor

The MSA Model 260/261 is a combination combustible gas and oxygen monitor. There are meter displays for both indicators. Visual and audible alarms for a % LEL reading and a low oxygen reading are included. The Model 261 also has a high oxygen reading alarm. The audible alarm can be deactivated. Air is drawn into the instrument by a battery-operated pump.

SETUP

1. Record the instrument serial number or ID number on the data sheet.
2. Attach the sampling hose to the instrument. Make sure that the connection is hand tight.

STARTUP

3. Turn the center "ON-OFF" control clockwise to the "HORN-OFF" position. Both meter pointers will move, both alarm lights will light, and the center green lamp will blink on and off. (*Note:* On the Model 261, the light will not turn on until after the reset button is pushed.) The green light indicates alarms status. When it glows continuously, the audible alarm is operable. When it blinks on and off, it indicates that the audible alarm has been deactivated.
4. Adjust the meter pointer on the % oxygen monitor by pulling and turning the "O₂ CALIBRATE KNOB." The knob is supplied with a clutch to prevent accidental field decalibration. Adjust the pointer to read 20.8%, which is the hatch mark below the 21% mark.
5. Adjust the meter pointer on the %LEL meter by pulling and turning the "LEL ZERO KNOB." Adjust the pointer to read 0%.
6. Press the red alarm "RESET" button to reset the alarms. Both red lights should stop flashing. (*Note:* The "RESET" button will not reset the alarms if the meter pointers exceed the alarm levels.)
7. Press the black "CHECK" button and observe the pointer on the %LEL meter. The pointer should move above 80% LEL into the BATTERY zone of the meter. This indicates that the battery is okay. If it does not reach the BATTERY zone, inform an instructor/technician.

LEAK TEST

8. Momentarily hold a finger over the sample inlet or end of sample probe. Observe that the flow indicator float (lower right hand corner of instrument face) drops out of sight, indicating

no flow. If the float does not drop out of sight, check the system for leaks. If the instrument does not pass the leak test, inform an instructor/technician.

ALARM CHECK

The purpose of these steps is to check the meter readings at which the alarms will sound.

9. Turn the O₂ CALIBRATE knob counterclockwise (decreasing the % oxygen reading) while watching the % oxygen meter and the oxygen alarm light. Note the reading at which the alarm sounds and the light starts flashing. Adjust the reading back to 20.8% and press the reset button. Record the reading on the data sheet. The lower alarm reading should be 19.5%.
10. **(MSA 261 only)** Turn the O₂ CALIBRATE knob clockwise (increasing the % oxygen reading) while watching the % oxygen meter and the oxygen alarm light. Note the reading at which the alarm sounds and the light starts flashing. Adjust the reading back to 20.8% and press the reset button. Record the alarm reading on the data sheet. The upper alarm reading should be 25%.
11. Turn the zero LEL knob clockwise until the alarm is activated. Record this reading. Return the meter pointer to zero and press the reset button. The alarm should have activated at 25% LEL.
12. If any of the alarm points are not what they should be, inform an instructor/technician.
13. The instrument is ready for calibration.

CALIBRATION

14. Open the clamp to the gas bag labeled "**PENTANE 0.75%**" and attach the sample line to the bag. Draw a sample into the instrument until a constant reading is obtained.
15. Record your reading on the data sheet. The instrument should give a reading of 50% LEL. Inform the instructor if it does not.
16. Disconnect the sample line and clamp the bag. Allow fresh air to flow through the instrument until the reading returns to zero. Rezero the instrument, if needed.

SAMPLING

17. Please note that the **Model 261** has a latching mechanism that engages the %LEL meter pointer if it reaches or exceeds 100. To disengage the lock, the instrument must be turned

off and then turned back on in an area where the LEL readings are less than 100%. Room air will do.

18. For field monitoring, the alarm should be in the operable mode. For this exercise, you may keep the audible alarm deactivated to reduce noise levels.
19. Sample each of the gas bags listed on the data sheet. Record the readings.

SHUTDOWN

20. When sampling is complete, flush fresh air through the instrument. Turn the instrument OFF.

STATION 2.

MSA Model 360 Combination CGI/O₂/CO Monitor

The MSA Model 360 is a combination combustible, oxygen, and carbon monoxide (CO) monitor. It has a digital display that shows only one reading. It has alarms for a specific % LEL reading, low and high oxygen, and a specific carbon monoxide reading. If the alarm levels are reached for any of these responses, there will be a visual and audible indication. This will occur no matter what function is being displayed at the time. The audible alarm can be deactivated. Air is drawn into the instrument by a battery-powered pump.

SETUP

1. Record the instrument serial number or ID number on the data sheet.
2. Attach the sampling hose to the instrument. Make sure the connection is hand tight.

STARTUP

3. Turn the FUNCTION control to the "HORN-OFF" position. Alarm signals will flash for all three chemicals, the "HORN OFF" green/yellow lamp will be off and % LEL will show in the readout.
4. A low battery condition is indicated by a BATT sign in the readout or by a steady horn. Inform an instructor/technician if this occurs.
5. Set the readout to zero (00) by lifting and turning the LEL ZERO knob. This must be done within 30 seconds of turning ON to prevent the possibility of activating the off-scale, LEL latching alarm.
6. Press the SELECT button firmly to obtain % OXY on the readout. Then set the readout to 20.8% by adjusting the OXY CALIBRATE knob.
7. Press the SELECT button firmly to obtain PPM TOX on the readout. Then set the readout to zero (00) by adjusting the TOX ZERO knob.
8. Press the RESET button. (*Note:* The "RESET" button will not reset the alarms if the exceed the alarm levels.) The "HORN OFF" green/yellow lamp will start flashing. The light indicates alarm status. When it glows continuously, the audible alarm is operable. When it blinks on and off, as it does now, it indicates that the audible alarm has been deactivated.

LEAK TEST

9. Momentarily hold a finger over the sample inlet or end of sample probe. Observe that the flow indicator float (lower right hand corner of instrument face) drops out of sight, indicating no flow. If the float does not drop out of sight, check the system for leaks. If the instrument does not pass the leak test, inform an instructor/technician.

ALARM CHECK

The purpose of these steps is to check the meter readings at which the alarms will sound.

10. Press the SELECT button until % LEL is displayed. Adjust the LEL ZERO knob until the alarm sounds. Record the % LEL reading. Set the reading back to zero and press the RESET button. The alarm should activate at 25%.
11. Press the SELECT button until OXY is displayed. Turn the OXY CALIBRATE knob counterclockwise (decreasing the % oxygen reading) until the alarm sounds. Record the % OXY reading. Adjust the reading back to 20.8% and press the RESET button. The lower alarm reading should be 19.5%.
12. Turn the OXY CALIBRATE knob clockwise (increasing the % oxygen reading) until the alarm sounds. Record the % OXY. Adjust the reading back to 20.8% and press the RESET button. The upper alarm reading should be 25%.
13. Press the SELECT button until TOX is displayed. Turn the TOX ZERO knob clockwise until the alarm is activated. Record this reading. Adjust the reading back to zero and press the RESET button. The alarm should have activated at 35 ppm.
14. If any of the alarm points are not what they should be, inform an instructor/technician.
15. Turn the FUNCTION control to MANUAL for continuous readout of any one gas or to SCAN for automatic scanning of the three gas readings. *Note:* All alarm functions operate in either position.
16. The instrument is ready for sampling.

CALIBRATION

17. Open the clamp to the gas bag labeled "PENTANE 0.75%" and attach the sample line to the bag. Draw a sample into the instrument until a constant reading is obtained.
18. Record your readings on the data sheet. The instrument should give a reading of 50% LEL. Consult the instructor for proper oxygen and carbon monoxide readings.
19. Disconnect the sample line and clamp the bag. Allow fresh air to flow through the instrument until the reading returns to zero. Rezero the instrument, if needed.

SAMPLING

20. For field monitoring, the alarm should be in the operable mode (SCAN or MANUAL setting). For this exercise, you may keep the audible alarm deactivated to reduce noise levels.
21. *Note:* The **Model 360** has a latching mechanism that engages if the % LEL exceeds 100. To disengage the lock, the instrument must be turned off and then turned back on in an area where the LEL readings are less than 100%. Room air will do.
22. Sample each of the gas bags listed on the data sheet. Record the readings.

SHUTDOWN

23. When done sampling, flush fresh air through the instrument. Turn the instrument OFF.

STATION 3

Gastech Model 1314 Gastechtor

The GasTech Model 1314 is a combination combustible, oxygen, and toxic monitor. There is no separate toxic sensor. The "toxic" response is provided by an amplification of the combustible sensor (supersensitive CGI). Thus the toxic response is actually ppm combustible. The readout is an analog meter that only displays one reading. The readout being displayed depends on the position of the buttons on the side of the instrument. It has a specific % LEL, low and high oxygen, and toxic level alarms. The oxygen alarm will sound even if % LEL is being displayed and vice versa. The toxic alarm, however, will only sound if in the "PPM" mode. The unit has a battery-powered pump for drawing air.

STARTUP

1. Attach the hose to instrument by means of the quick release fitting.
2. Put the PPM/LEL switch in the LEL (out) position, with the black indicator showing, and OXY/LEL switch also in the LEL (out) position.
3. Press the POWER switch to turn the instrument on, with orange indicator dot showing. The meter will normally rise upscale and a pulsing or steady alarm signal may sound. Audible hum of pump will be noticed. The cause of the alarm condition (combustibles, oxygen, or both) can be identified by the blinking lights.
4. Press the BATT CK button and note the meter reading. If reading is close to or below the BATT CHECK mark on the meter, consult an instructor/technician.
5. Allow the instrument to warm up until the meter stabilizes (about a minute). If a pulsed oxygen alarm continues to sound, turn the OXY CAL potentiometer clockwise to stop it. If the sound is steady, turn the potentiometer counterclockwise.
6. With the hose inlet in a clean air location, turn the ZERO LEL potentiometer to bring the meter to "0" indication. If this is not possible, consult an instructor/technician.
7. Put the OXY/LEL switch in the OXY (in) position, so that the orange indicator shows. Turn the OXY CAL potentiometer to bring the meter to the O₂ CAL mark (21 %).
8. As a quick check, gently breathe into hose inlet and allow instrument to sample exhaled air. Reading should come down to about 16%, and alarm should sound at 19.5%. Allow it to return to 21 %, then put switch back in LEL position.
9. These particular units have a high oxygen alarm that will sound in a steady tone and the amber alarm lights will blink when reading reaches or exceeds 25%.

10. The instrument will automatically test for oxygen whenever it is used, and will give a pulsed audible and an amber light alarm if oxygen content drops to 19.5%. It is not necessary to use the instrument with the switch in the OXY position unless oxygen measurements are of primary interest. If both abnormal gas conditions exist simultaneously, both lights will blink in their normal pattern, but alarm will sound continuously.
11. For readings in the 0-100% LEL range, hold inlet at point to be tested. Watch meter and observe maximum reading as taken from the upper set of graduations, 0-100% scale. If reading rises above the alarm setting (20% LEL), a pulsed red light and an audible alarm will commence, and will continue as long as reading remains above alarm point.
12. If the reading on the 0-100% range is imperceptible or very small, use the sensitive range, 0-500 ppm. First allow to warm up in the LEL range, and then push range switch to put circuit in PPM range (colored indicator showing). Rezero carefully with the ZERO LEL potentiometer.

Because of the very high sensitivity of this range, the meter will tend to drift until instrument is thoroughly warmed up. Always let it run for 5 minutes or more, whenever possible, before operating on the PPM range. Take the reading immediately after zeroing, and observe maximum deflection as taken from the middle set of graduations, 0-500 PPM scale. The alarm will sound whenever the reading rises above the preset alarm level - 100 ppm.

CALIBRATION

13. Put the PPM/LEL switch in the LEL (out) position.
14. Unclamp the bag labeled "HEXANE 0.55%" and attach it to the sample inlet. Record the reading when it has stabilized. The reading should be 50%. If not, please inform the instructor.

SAMPLING

15. Sample each of the gas bags listed on the data sheet. Record the readings. **DO NOT USE THE PPM SETTING UNLESS THE LEL RESPONSE IS VERY LOW.**

SHUTDOWN

16. When sampling is complete, flush fresh air through the instrument. Turn the instrument OFF.

DATA SHEET

	STATION 1			STATION 2			STATION 3				
	MSA 260/261			MSA 360			GASTECH 1314				
SAMPLE BAGS	ID #:			ID #			ID #				
	O ₂	LEL		O ₂	LEL	CO	O ₂	LEL	O ₂	LEL	PPM
ALARM LEVELS*											
PENTANE CAL GAS											
HEXANE CAL GAS											
BAG 1											
BAG 2											
BAG 4											
BAG 5											
BAG 6											

*The two spaces under O₂ are for the low and high level alarm readings.

QUESTIONS

1. Did the alarms activate at the appropriate readings? Which instruments did not?
2. Why do the different instruments give different responses to similar combustible gases?
3. What are the hazards (if any) associated with each unknown bag?

4. List the limitations and advantages of each instrument for monitoring an unknown atmosphere.

MSA 260/261:

MSA 360:

GasTech 1314:

EXERCISE #2

Photoionization Detectors - Survey

OBJECTIVE

Participants will learn how to calibrate and operate the HNU Model PI-101 Photoionization Detector.

PROCEDURE

Students will divide into groups as directed by the laboratory instructor. Each group will have an HNU PI-101 Photoionization Detector with either a 10.2 eV or 11.7 eV lamp, and eight gas bags. Also, five containers with unknown chemicals will be placed around the room.

STATION 1:	Bag A	100 parts per million (ppm) toluene
	Bag B	100 ppm acetone
	Bag C	100 ppm toluene/100 ppm acetone
	Bag D	800 ppm acetone
	Bag E	250 ppm acetone
	Bag F	50 ppm acetone
	Bag G	50 ppm hexane
	Bag CH ₄	100 ppm methane

STATION 2: Five containers with unknowns

By following the instructions, sample each station and record your results. A discussion of your findings will be held at the end of the exercise.

SETUP

1. Record the instrument serial number or ID number on the data sheet.
2. Record the lamp energy.

STARTUP

Refer to **Figure 1** for location of instrument controls.

3. Connect the probe.
4. Turn the FUNCTION SWITCH to the BATTERY CHECK position. The needle should deflect within or above the green arc. If not, inform the instructor. If the red indicator light (low battery) comes on, do not use the instrument.
5. To ensure that the lamp will light, turn the FUNCTION switch to any RANGE setting and place a solvent based marker near the sample intake on the probe. A needle deflection should occur, thus indicating that the lamp is on.
6. There are two methods of zeroing an instrument. For this lab, use METHOD 1.
 - METHOD 1 - Turn the FUNCTION SWITCH to the STANDBY position and zero the instrument using the ZERO knob. This procedure is used to zero the instrument electronically. If the SPAN setting is altered, the zero should be rechecked and adjusted. Wait fifteen to twenty seconds to ensure that the zero reading is stable. If necessary, readjust the zero.
 - METHOD 2 - Turn the FUNCTION SWITCH to the range being used and rotate the ZERO knob until the meter reads zero. Now you have zeroed out background. If the SPAN setting is changed after the zero is set, the zero should be rechecked and adjusted.

You are now ready to calibrate your instrument.

CALIBRATION

7. The instructor will assist the students in the calibration procedure. A compressed gas cylinder containing isobutylene will be used to calibrate the instrument. Set the FUNCTION SWITCH to the 0-200 RANGE setting.
8. Connect the probe to the tubing from the ISOBUTYLENE cylinder. Unlock the SPAN knob by moving the black lock handle counter clockwise. By adjusting the SPAN setting between 0-100, obtain the appropriate instrument reading. The instructor will tell you the

appropriate reading. Do not lock the SPAN knob at all during this lab exercise. Record the SPAN setting at calibration on the data sheet.

SAMPLING

9. When taking readings, adjust the FUNCTION SWITCH to get the maximum on scale needle deflection. If the reading exceeds the meter range, adjust the FUNCTION SWITCH.
10. Measure for contaminants in BAGS A, B, C, G, and CH₄ and record the results.
11. Take readings over the openings of each of the unknown containers. Record the readings.

CALIBRATION CHANGE

12. By adjusting the SPAN, calibrate the instrument to BAG B (acetone). Measure the concentration of BAGS C, D, E, and F and record your results. Then plot the instrument readings vs. actual concentration from BAGS B, D, E, and F on **Graph 1**.

SHUTDOWN

13. Turn the FUNCTION SWITCH to the OFF position.

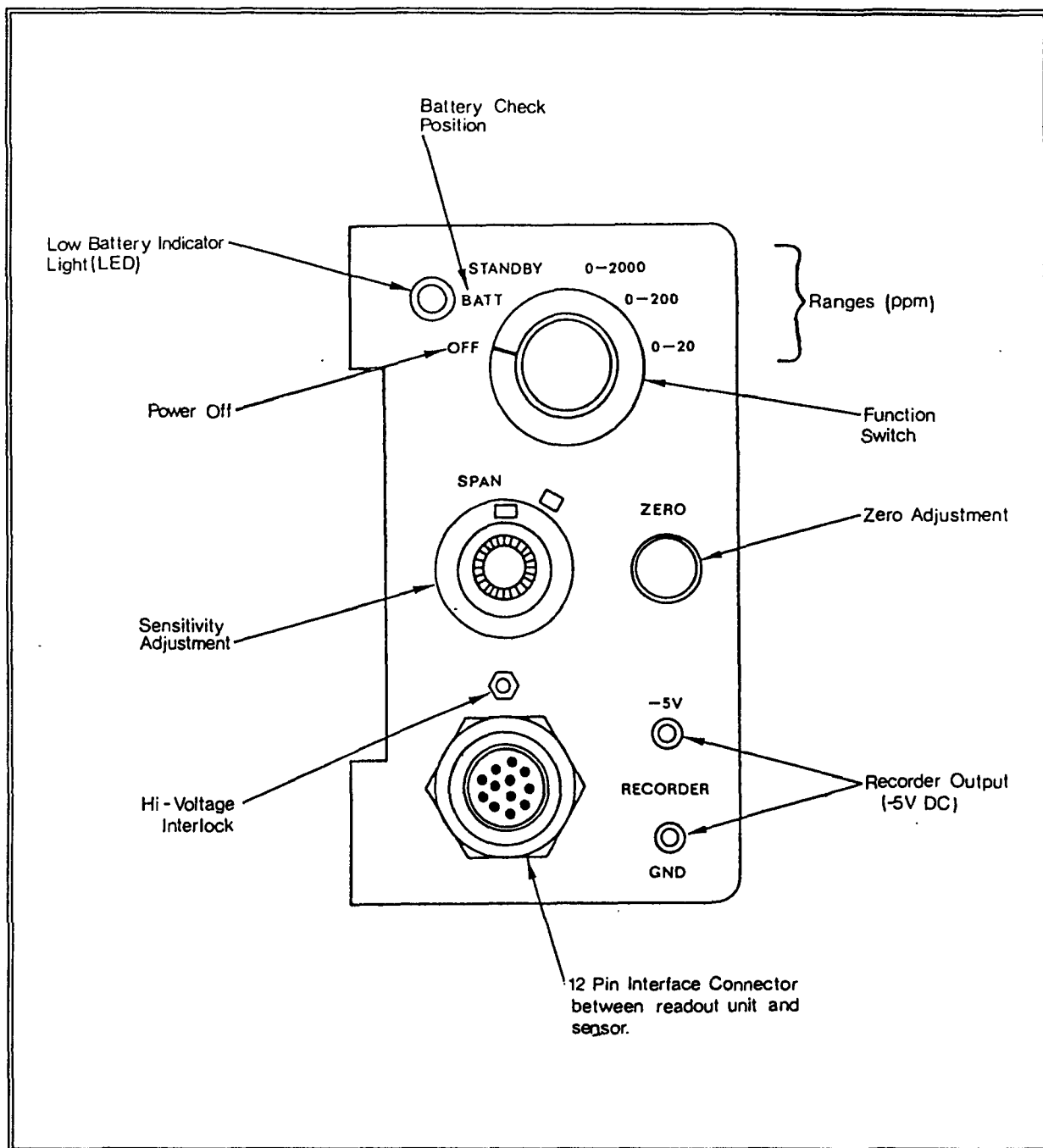


FIGURE 1. HNU PI 101 CONTROLS

Source: *Instruction Manual for Model PI 101 Photoionization Analyzer*, 1975, HNU Systems, Inc. Used with permission of HNU Systems, Inc.

DATA SHEET

TABLE 1	
INSTRUMENT MODEL	
I.D. NUMBER	
LAMP ENERGY	
CALIBRATION	
GAS	
CONCENTRATION	
INSTRUMENT READING	
SPAN SETTING	

TABLE 2			
BAG	CONCENTRATION	INSTRUMENT READING	RELATIVE RESPONSE*
A - TOLUENE	100 ppm		
B - ACETONE	100 ppm		
C - TOLUENE/ ACETONE	100/100		
G - HEXANE	50 ppm		
CH ₄ - METHANE	100 ppm		

* Relative Response = Instrument Reading ÷ Actual Concentration. Multiply by 100% to get % Relative Response.

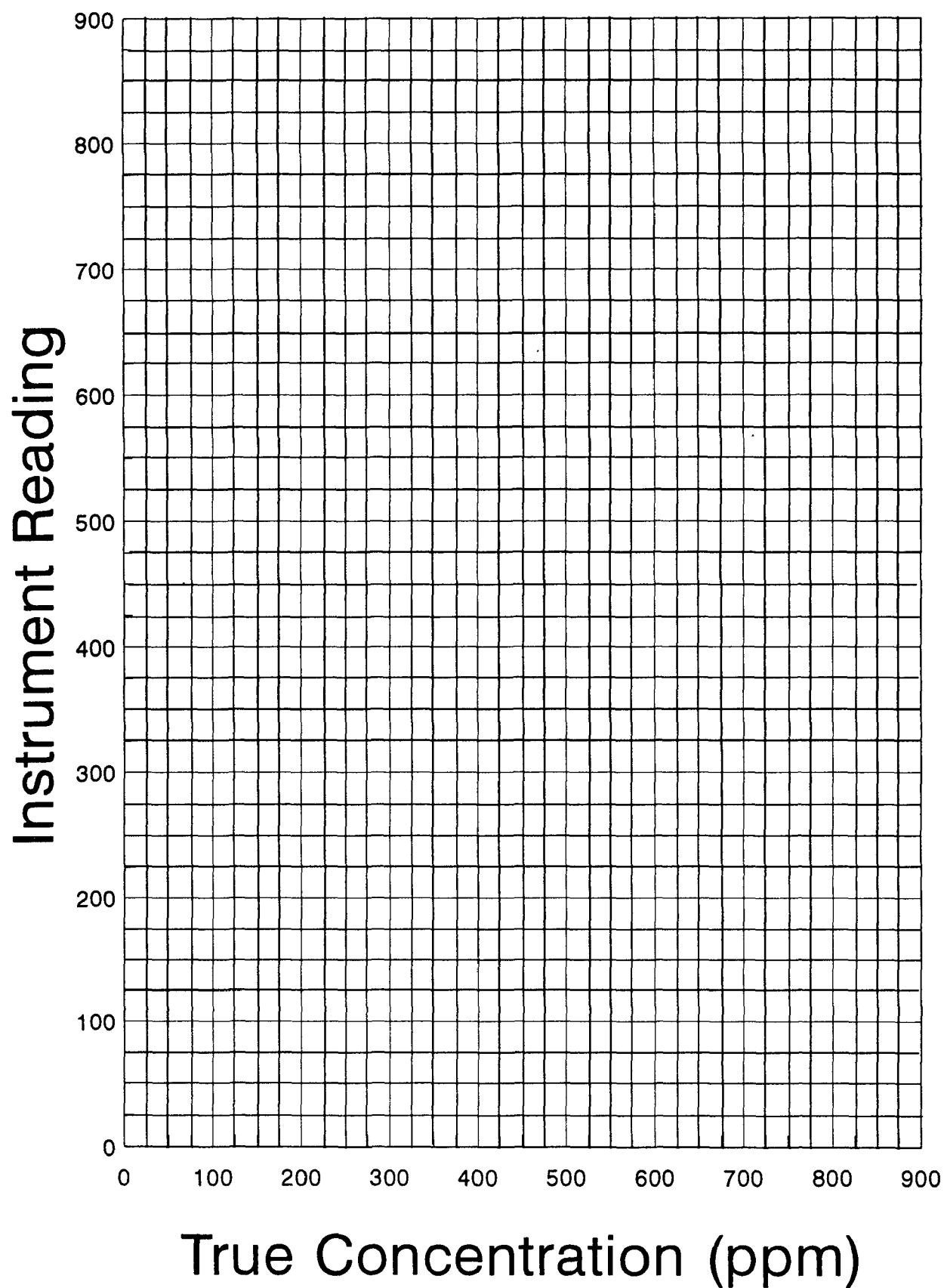
DATA SHEET

TABLE 3	
SAMPLE LOCATION*	READING
1	
2	
3	
4	
5	

*Add information about location of probe when taking the reading.

TABLE 4 ACETONE CALIBRATION			
BAG	ACTUAL CONCENTRATION	INSTRUMENT READING	SPAN SETTING
B	100 ppm		
C	100/100		
D	800 ppm		
E	250 ppm		
F	50 ppm		

GRAPH 1. INSTRUMENT READING VS. TRUE CONCENTRATION



QUESTIONS

1. Calculate and record the relative response for each of the chemicals in **Table 2**.
2. Why is the reading for Bag C in **Table 2** different from the reading in **Table 4**?
3. From **Graph 1**, does the instrument accurately measure all four concentrations? If you were going to measure acetone vapors at concentrations of 0–10 ppm, would this calibration curve be of value to you?
4. Unknown 2 is found to be acetone. Develop a method(s) using the HNU to determine the concentration of acetone at the location.
5. You are using an HNU to survey a site and obtain a reading of 200. How do you report your findings and what additional information would you like recorded?

EXERCISE #3

Flame Ionization Detectors - Survey

OBJECTIVE

Participants will learn how to calibrate and operate the Foxboro Organic Vapor Analyzer OVA-128 in the survey mode.

PROCEDURE

Students will divide into groups as directed by the laboratory instructor. Each group will have an Foxboro OVA-128 plus eight gas bags. Also, five containers with unknown chemicals will be placed around the room.

Station 1:	Bag A	100 parts per million (ppm) toluene
	Bag B	100 ppm acetone
	Bag C	100 ppm acetone/100 ppm toluene
	Bag D	800 ppm acetone
	Bag E	250 ppm acetone
	Bag F	50 ppm acetone
	Bag G	50 ppm hexane
	Bag CH ₄	100 ppm methane

Station 2: Five sampling containers

By following the instructions, sample each station and record your results. A discussion of your findings will be held at the end of the exercise.

Please read each paragraph completely before following the directions and proceeding to the next paragraph.

SETUP

1. Record the instrument serial number or ID number on the data sheet.

STARTUP

2. Turn off the charger and disconnect the charger cable from the instrument.
3. Unlock the GAS SELECT dial and adjust it to 300 (i.e., a 3 in the window and 00 on the dial).
4. Turn the VOLUME knob fully counter clockwise.
5. Ensure that the SAMPLE INJECT VALVE and BACK FLUSH VALVE are in the full out position.
6. The toggle switches on this instrument have a lock to prevent accidental changes. To move the toggle switch, lift and then move the lever.
7. Move the INSTRUMENT switch to ON and allow 5 minutes for warm-up.
8. Move the PUMP switch to ON. You should hear the pump running. Place the instrument in a vertical position and look at the SAMPLE FLOW RATE (rotameter at lower left of panel). The flow rate (read at center of ball) should be 2.0 (liters/minute). A reading between 1.5 and 2.5 is considered adequate.
9. Set the CALIBRATE switch to X10. Adjust the CALIBRATE knob until the meter reads 0.
10. Open the H₂ TANK VALVE and H₂ SUPPLY VALVE one and one-half turns counter clockwise. The TANK gauge should be 500 psi or higher. The SUPPLY gauge should read between 10 and 12 psi. If they do not, inform the instructor.
11. Wait about 1 minute. Depress the red IGNITER BUTTON (on the side of the pack) until the flame ignites or until 6 seconds have passed. Flame ignition is indicated by a sharp meter needle deflection towards 10 along with a small "pop" sound. Also, the meter needle should return to a reading above 0 instead of 0. Do not depress the button longer than 6 seconds. If the flame does not ignite on the first try, wait a minute, and try again. If it does not ignite on a second try, check that steps 1 through 10 have been completed. Then consult an instructor or technician for assistance.
12. Use the CALIBRATE knob to adjust the meter reading to zero. Move the CALIBRATE switch to X1 and rezero.

CALIBRATION

13. Set the CALIBRATE switch to X10.
14. Locate the METHANE calibration gas bag. Methane is the normal calibration gas for the OVA.
15. Open the bag clamp and attach the methane bag to the probe inlet. It is important that the bag be open before attaching it so that a "flame out" does not occur from oxygen starvation.
16. Unlock and adjust the GAS SELECT knob so that the meter reading is equal to the bag concentration divided by the CALIBRATE switch setting. For example, if the bag concentration is 90 ppm, then the reading should be 9 (90 divided by 10).
17. Disconnect the gas bag and close the clamp.
18. The GAS SELECT setting should be about 300. 300 is the "ideal" setting, but your instrument may have a different reading. If the setting must be adjusted above 400 or below 200, internal calibration may be advisable.
19. The instrument is now calibrated to methane and ready for survey purposes.

SAMPLING

20. During the next two steps, change the CALIBRATE switch setting as necessary to get the maximum on-scale reading. If the meter reads above 10 on the X100 setting, report the reading as greater than 1000.
21. Take readings of bags A, B, C and G. Record the data.
22. Take readings at the five containers. Record the readings and locations.

CALIBRATION

23. Change the CALIBRATE switch to X10.
24. Open and connect Bag B to the probe inlet. Adjust the GAS SELECT knob until the instrument reads 10 on the X10 range.
25. Disconnect and close the bag. Use the CALIBRATE ADJUST knob to rezero, if needed.
26. Take readings of bags C, D, E, and F. Record the readings. Plot the readings from bags B, D, E, and F on GRAPH 1.

SHUTDOWN

27. Close the H₂ SUPPLY valve, then the H₂ TANK valve.
28. Move the INSTRUMENT switch to OFF.
29. When the SUPPLY pressure gauge falls to zero, move the PUMP switch to OFF.

DATA SHEET

TABLE 1	
INSTRUMENT MODEL	
I.D. NUMBER	
CALIBRATION	
GAS	
CONCENTRATION	
INSTRUMENT READING	
GAS SELECT SETTING	

TABLE 2			
BAG	CONCENTRATION	INSTRUMENT READING	RELATIVE RESPONSE*
A - TOLUENE	100 ppm		
B - ACETONE	100 ppm		
C - TOLUENE/ ACETONE	100/100		
G - HEXANE	50 ppm		

*Relative Response = Instrument Reading ÷ Actual Concentration. Multiply by 100% to get % Relative Response.

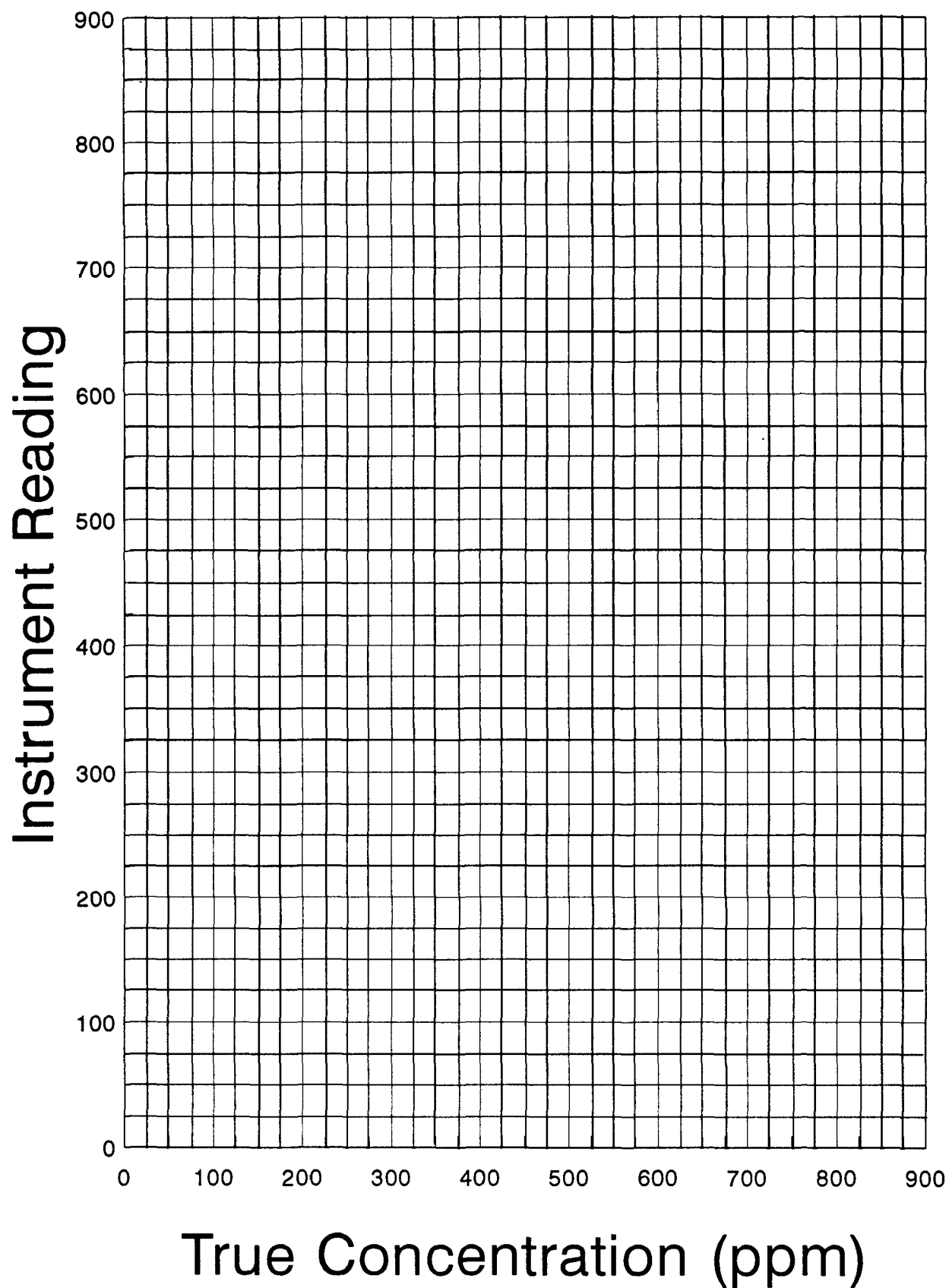
DATA SHEET

TABLE 3	
SAMPLE LOCATION*	READING
1	
2	
3	
4	
5	

* Add information about location of probe when taking the reading.

TABLE 4 ACETONE CALIBRATION			
BAG	ACTUAL CONCENTRATION	INSTRUMENT READING	GAS SELECT SETTING
B	100 ppm		
C	100/100		
D	800 ppm		
E	250 ppm		
F	50 ppm		

GRAPH 1. INSTRUMENT READING VS. ACTUAL CONCENTRATION (from Table 4)



QUESTIONS

1. Calculate the relative response for each of the chemicals in **Table 2**.
2. Why is the reading for Bag C in **Table 2** different from the reading in **Table 4**?
3. From **Graph 1**, does the instrument accurately measure all four concentrations? If you were going to measure acetone vapors at concentrations of 0–10 ppm, would this calibration curve be of value to you?
4. Unknown 2 is found to be acetone. Develop a method(s) using the OVA to determine the concentration of acetone at the location.
5. You are using an OVA to survey a site and obtain a reading of 200. How do you report your findings and what additional information would you like recorded?

EXERCISE #4

Gas Chromatography - Organic Vapor Analyzer

OBJECTIVE

Participants will learn how to operate the Foxboro OVA-128 with gas chromatograph option as a portable gas chromatograph.

PROCEDURE

The students will divide into groups as directed by the laboratory instructor. Each group will have a Foxboro OVA-128 with gas chromatograph option and three gas bags.

Bag CH ₄ :	Calibration gas
Bag C:	Standard of 100 ppm toluene and 100 ppm acetone
Unknown #1	

By following the instructions of the lab manual and instructor, each group will produce a gas chromatograph for each bag. By comparing the results from the standard to the unknown, the group will try to determine what chemicals are present and at what concentrations. The results will be recorded and discussed at the end of the exercise.

Please read each paragraph completely before following the directions and proceeding to the next paragraph.

SETUP

1. Record the instrument serial number or ID number on the data sheet.

STARTUP

2. For gas chromatograph use, the charger can remain on and connected to the OVA.
3. Unlock the GAS SELECT dial and adjust it to 300 (i.e., a 3 in the window and 00 on the dial).
4. Turn the VOLUME knob fully counter clockwise.
5. Ensure that the SAMPLE INJECT VALVE and BACK FLUSH VALVE are in the full out position.
6. The toggle switches on this instrument have a lock to prevent accidental changes. To move the toggle switch, lift and then move the lever.
7. Move the INSTRUMENT switch to ON and allow 5 minutes for warm-up.
8. Move the PUMP switch to ON. You should hear the pump running. Place the instrument in a vertical position and look at the SAMPLE FLOW RATE (rotameter at lower left of panel). The flow rate (read at center of ball) should be 2.0 (liters/minute). A reading between 1.5 and 2.5 is considered adequate.
9. Set the CALIBRATE switch to X10. Adjust the CALIBRATE knob until the meter reads 0.
10. Open the H₂ TANK VALVE and H₂ SUPPLY VALVE one and one-half turns counter clockwise. The TANK gauge should be 500 psi or higher. The SUPPLY gauge should read between 10 and 12 psi. If they do not, inform the instructor.
11. Wait about 1 minute. Depress the red IGNITER BUTTON (on the side of the pack) until the flame ignites or until 6 seconds have passed. Flame ignition is indicated by a sharp meter needle deflection toward 10 along with a small "pop" sound. Also, the meter needle should return to a reading above 0 instead of 0. Do not depress the button longer than 6 seconds. If the flame does not ignite on the first try, wait a minute, and try again. If it does not ignite on a second try, check that steps 1 through 10 have been completed. Then consult an instructor or technician for assistance.
12. Use the CALIBRATE knob to adjust the meter reading to zero. Move the CALIBRATE switch to X1 and rezero.

CALIBRATION

13. Set the CALIBRATE switch to X10.
14. Locate the METHANE calibration gas bag. Methane is the normal calibration gas for the OVA.
15. Open the bag clamp and attach the methane bag to the probe inlet. It is important that the bag be open before attaching it so that a "flame out" does not occur from oxygen starvation.
16. Unlock and adjust the GAS SELECT knob so that the meter reading is equal to the bag concentration divided by the CALIBRATE switch setting. For example, if the bag concentration is 90 ppm, then the reading should be 9 (90 divided by 10).
17. Disconnect the gas bag and close the clamp.
18. The GAS SELECT setting should be about 300. 300 is the "ideal" setting, but your instrument may have a different reading. If the setting must be adjusted above 400 or below 200, internal calibration may be advisable.

GAS CHROMATOGRAPH SETUP

19. Connect the strip chart recorder to the OVA. Move the HI/LO switch (on the side of the recorder) to the LO position. The chart paper should start moving and you should hear a clicking sound. If the chart does not operate, check the cable connections. Inform the instructor if the chart doesn't work.
20. Turn the ZERO knob on the recorder (next to HI/LO switch) completely clockwise.
21. Turn the OVA CALIBRATE knob to adjust the baseline (black line produced by the pin) on the chart. Do not use the ZERO knob on the recorder. The baseline should be about 1/4 inch (two thin brown lines) above the thick brown line next to the sprocket holes.
22. Locate the stopwatch. Practice with the stopwatch until you can do lap counting. The instructor will demonstrate. Lap counting involves stopping the readout without stopping the stopwatch timing. This is useful for timing more than one peak.

STANDARD CHROMATOGRAM

23. Open and connect the STANDARD (Bag C: Acetone/Toluene) bag to the probe inlet. Watch the meter needle. When the needle has deflected to its highest point, depress the SAMPLE INJECT VALVE and start the stopwatch. Disconnect and close the gas bag. If the needle passes 10, wait 3 seconds, then depress the INJECT VALVE.

Keep the SAMPLE INJECT VALVE depressed until the end of the chromatogram. The instructor will discuss how to determine when the chromatogram is done.

24. Strike a line across the chart with a pen or pencil to indicate the start of a chromatogram. Write the OVA CALIBRATE SWITCH setting (X1, X10, X100) and the recorder HI/LO setting on the chart paper.
25. Watch the chart paper or meter face for an upward needle deflection. When the needle reaches a maximum reading and starts to drop, note the time. This is the top of the peak and the time is the **retention time** for the peak. Do this for each peak. Record the retention times for each peak.
26. If a peak is too small or goes off scale, you will need to rerun the standard at a different CALIBRATE SWITCH setting and/or different HI/LO setting. **Table 1** shows the relationship between peak size and instrument settings. For example, if a peak is off scale on a HIX10 setting, changing the settings to LOX10 or HIX100 would make the peaks 1/2 or 1/10 the size of the original peaks.

TABLE 1		
RECORDER RANGE FACTOR	OVA SCALE	RELATIVE PEAK SIZE
HI	X1	1
LO	X1	1/2
HI	X10	1/10
LO	X10	1/20
HI	X100	1/100
LO	X100	1/200

27. When a chromatogram is done (i.e, the last peak is out and the baseline is back to normal), lift the SAMPLE INJECT VALVE. The instrument is ready for another run.

SAMPLE CHROMATOGRAM

28. Repeat steps 22 through 26 using the UNKNOWN sample bag.

SHUTDOWN

29. Close the H₂ SUPPLY valve, then the H₂ TANK valve.
30. Move the INSTRUMENT switch to OFF.

31. Move the RECORDER RANGE SETTING switch to OFF.
32. When the SUPPLY pressure gauge falls to zero, move the PUMP switch to OFF.

CALCULATIONS FOR QUALITATIVE EVALUATION

27. (Optional) Tear off the strip chart and measure the distance from the injection point to the middle of the peak in mm (see Figure 1 below).

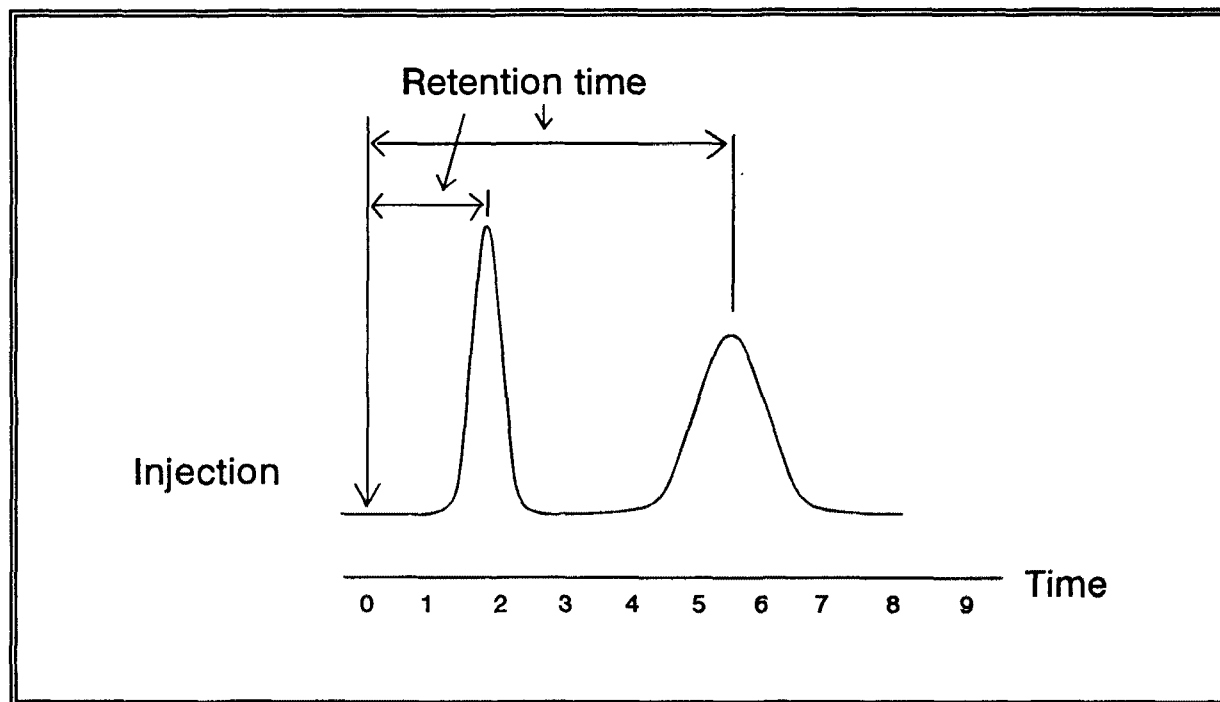


FIGURE 1. RETENTION TIME (DISTANCE) ILLUSTRATION

28. Compare the retention times of the known standard and the unknown. If the retention times are relatively close, then the unknown can possibly be identified through comparison to the known. For example, if a standard of acetone released at 144 seconds and a peak on our unknown was at 136 seconds, then we can assume that the peak was acetone.

QUANTITATIVE ANALYSIS

29. To find the concentration of a chemical that has been identified with a standard, you will need a ruler, a calculator, and a pencil.
30. Draw a triangle that approximates the area of the curve similar to the example (Figure 2) below.

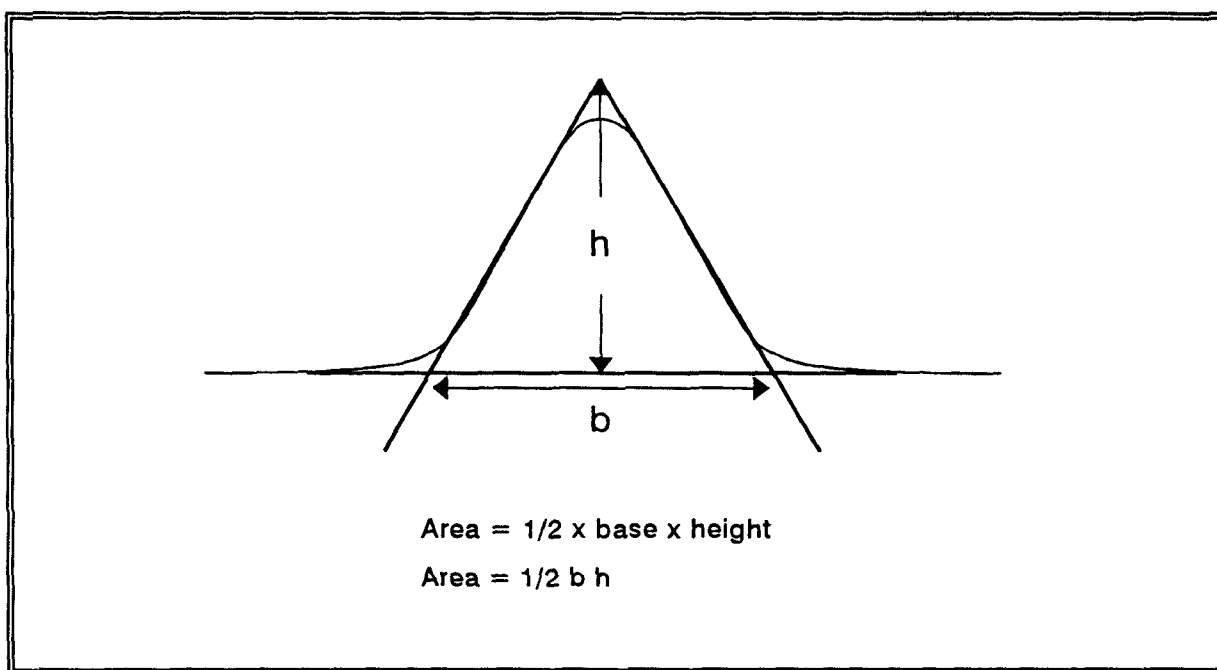


FIGURE 2. PEAK AREA ILLUSTRATION

31. Calculate the area of the triangle for the standards and unknowns by using the following formula:

$$\text{Area} = \frac{1}{2}(b)(h)$$

32. To compensate for the different instrument settings a **corrected area** formula must be used:

$$\text{Corrected Area} = \text{OVA Setting} \times \text{Recorder Range Factor} \times \text{Area of Triangle}$$

X100
 X10
 X1

HI = .5
 LO = 1.0

33. To obtain the actual concentration of the unknown, divide the corrected area of the unknown by the corrected area of the standard and multiply by the standard concentration.

$$\text{Concentration of unknown} = \frac{\text{Corrected Area}_{\text{unknown}}}{\text{Corrected Area}_{\text{standard}}} \times \text{Standard concentration}$$

TABLE 2					
	STANDARD BAG C		UNKNOWN #1		
	ACETONE	TOLUENE	PEAK 1	PEAK 2	PEAK 3
CONCENTRATION					
RETENTION TIME					
RETENTION DISTANCE (mm)					
PEAK BASE (mm)					
PEAK HEIGHT (mm)					
PEAK AREA (mm ²)					
OVA SCALE SETTING					
RECORDER SETTING					
CORRECTED AREA (mm ²)					

CALCULATIONS

QUESTIONS

1. Identify the peaks in Unknown #1. For the peaks that can not be positively identified, list the possible candidates.
2. What are the concentrations of the identified peaks? Compare your numbers with the actual concentrations (from the instructor). Give reasons why your results may vary from the actual concentrations.

CHROMATOGRAPHY AND SURVEY GUIDE
FOXBORO CENTURY ORGANIC VAPOR ANALYZERS

COMPOUND	T-12 COLUMN				G-24 COLUMN		SYNONYM
	TWA ppm	RR %	tR' sec	α	tR' sec	α	
ACETONE	750	82	118	2.23	36	0.29	2-PROPANONE
ACETONITRILE	40	64	384	7.25	39	0.32	
ACRYLONITRILE	2	98	252	4.75	45	0.37	VINYL CYANIDE
ALLYL ALCOHOL	2	27	623	11.75	98	0.80	
ALLYL CHLORIDE	1	45	36	0.68	38	0.31	
BENZENE	1	185	116	2.19	142	1.15	
BROMOETHANE	200	72	23	0.43	35	0.28	ETHYL BROMIDE
BROMOMETHANE	5	23	13	0.25	14	0.11	METHYL BROMIDE
BROMOPROPANE	*	73	51	0.96	100	0.81	PROPYL BROMIDE
BUTADIENE,1,3-	1000	36	3	0.06	7	0.06	BUTADIENE
BUTANE	800	58	12	0.23	3	0.02	
BUTANOL	100	46	725	13.68	243	1.98	BUTYL ALCOHOL
BUTANOL,2-	100	55	340	6.42	131	1.07	sec-BUTYL ALCOHOL
BUTANONE,2-	200	75	203	3.83	93	0.76	METHYL ETHYL KETONE
BUTENE	*	43	5	0.09	12	0.10	
BUTYL ACETATE	150	67	572	10.79	782	6.36	
BUTYL ACRYLATE	10	60	1099	20.74	1577	12.82	
BUTYL ACRYLATE,tert-	*	75	293	5.53	567	4.61	2-BUTYL ACRYLATE / PROPYLENE
BUTYL FORMATE	*	48	338	6.38	319	2.59	
BUTYL FORMATE,tert-	*	64	111	2.09	112	0.91	2-BUTYL FORMATE
BUTYL METHACRYLATE	*	60	1600	30.19	3950	32.11	
BUTYL METHYL ETHER,tert-	*	57	21	0.40	70	0.57	
CARBON TETRACHLORIDE	10	8	41	0.77	143	1.16	
CHLOROBENZENE	75	179	713	13.45	866	7.04	MONOCHLOROBENZENE
CHLOROFORM	2	57	122	2.30	91	0.74	TRICHLOROMETHANE
CHLOROMETHANE	50	56	4	0.08	5	0.04	METHYL CHLORIDE
CHLOROPROPANE	*	79	25	0.47	48	0.39	PROPYL CHLORIDE
CHLOROPROPANE,2-	*	55	13	0.25	26	0.21	ISOPROPYL CHLORIDE
CUMENE	50	18	690	13.02	1910	15.53	ISOPROPYL BENZENE
CYCLOHEXANE	300	92	16	0.30	161	1.31	HEXAMETHYLENE
CYCLOHEXANONE	25	43	—	0.00	1256	10.21	
DECANE	*	69	225	4.25	—	0.00	
DIACETONE ALCOHOL	50	56	950	17.92	1017	8.27	4-HYDROXY-4-METHYL-2-PENTANON
DIBROMOETHANE,1,2-	20	56	1168	22.04	536	4.36	ETHYLENE DIBROMIDE
DICHLOROBENZENE,1,2-	50	119	4060	76.60	—	0.00	o-DICHLOROBENZENE
DICHLOROETHANE,1,1-	100	70	66	1.25	66	0.54	
DICHLOROETHANE,1,2-	1	89	289	5.45	124	1.01	ETHYLENE DICHLORIDE
DICHLOROETHYLENE,1,1-	1	49	11	0.21	36	0.29	VINYLDENE CHLORIDE
DICHLOROETHYLENE,trans-1,2	200	40	37	0.70	55	0.45	
DICHLOROMETHANE	100	84	73	1.38	43	0.35	METHYLENE CHLORIDE
DICHLOROPROPANE,1,2-	75	96	258	4.87	203	1.65	PROPYLENE DICHLORIDE
DICHLOROPROPANE,1,3-	*	76	677	12.77	397	3.23	
DIOXANE,p-	25	28	760	14.34	242	1.97	DIETHYLENE DIOXIDE

COMPOUND	T-12 COLUMN				G-24 COLUMN		SYNONYM
	TWA ppm	RR %	tR' sec	α	tR' sec	α	
ENFLURANE	*	146	79	1.49	29	0.24	2-CHLORO-1,1,2-TRIFLUOROETHYL-DI-
ETHANE	*	77	1	0.02	1	0.01	FLUOROMETHYL ETHER / ETHRANE
ETHANETHIOL	0.5	28	24	0.45	31	0.25	ETHYL MERCAPTAN
ETHANOL	1000	20	178	3.36	45	0.37	ETHYL ALCOHOL
ETHENE	*	47	1	0.02	1	0.01	ETHYLENE
ETHER	400	47	13	0.25	38	0.31	DIETHYL ETHER
ETHYL ACETATE	400	67	143	2.70	108	0.38	
ETHYL ACRYLATE	5	71	263	4.96	254	2.07	
ETHYL BENZENE	100	111	495	9.34	1054	8.57	
ETHYL BUTYRATE	*	91	398	7.51	588	4.78	
ETHYL FORMATE	100	44	78	1.47	43	0.35	
ETHYL METHACRYLATE	*	73	375	7.08	514	4.18	
ETHYL PROPIONATE	*	83	241	4.55	274	2.23	
ETHYLENE OXIDE	1	49	31	0.58	35	0.23	EPOXYETHANE
FREON-11	1000	7	4	0.03	24	0.20	FLUOROTRICHLOROMETHANE
FREON-113	1000	91	8	0.15	43	0.35	TRICHLOROTRIFLUOROETHANE
FREON-114	1000	110	3	0.06	8	0.07	1,2-DICHLORO-1,1,2,2-TETRAFLUOROET
FREON-123	100	86	19	0.36	22	0.18	2,2-DICHLORO-1,1,1-TRIFLUOROETHA
FREON-12	1000	13	3	0.06	5	0.04	DICHLORODIFLUOROMETHANE
FREON-21	10	71	20	0.38	17	0.14	DICHLOROFUOROMETHANE
FREON-22	1000	67	5	0.09	3	0.02	CHLORODIFLUOROMETHANE
HALOTHANE	*	49	53	1.00	51	0.41	2-BROMO-2CHLORO-1,1,1,2,2,2-TRIFLUOROET
HEPTANE	400	80	16	0.30	232	1.89	
HEXADECANE	*	52	1764	33.28	—	0.00	
HEXAFLUOROPROPENE	*	81	1	0.02	2	0.02	PERFLUOROPROPENE
HEXANE	50	70	7	0.13	88	0.72	
ISOBUTANE	*	70	3	0.06	14	0.11	2-BUTANE / 2-METHYL PROPANE
ISOBUTENE	*	64	2	0.04	10	0.08	ISOBUTYLENE / 2-METHYL PROPENE
ISOPRENE	*	59	9	0.17	32	0.26	2-METHYL-1,3-BUTADIENE
ISOPROPYL ACETATE	250	71	155	2.92	180	1.46	
METHANE	*	100	1	0.02	1	0.01	
METHANOL	200	10	139	2.62	64	0.52	METHYL ALCOHOL
METHYL ACETATE	200	46	93	1.75	49	0.40	
METHYL ACRYLATE	10	39	197	3.72	107	0.87	
METHYL CYCLOHEXANE	400	67	20	0.38	230	2.23	
METHYL CYCLOPENTANE	*	81	9	0.17	114	0.93	
METHYL ISOBUTYL KETONE	50	82	468	8.33	353	2.37	4-METHYL-2-PENTANONE / HEXONE
METHYL METHACRYLATE	100	54	291	5.49	266	2.16	
METHYL SULFIDE	*	20	27	0.51	35	0.28	DIMETHYL SULFIDE
NITROMETHANE	100	35	1053	19.37	73	0.59	
NITROPROPANE	25	65	1893	35.72	285	2.32	
NITROPROPANE,2-	10	71	1030	19.43	191	1.55	
NONANE	200	85	103	1.94	1939	15.76	
OCTANE	300	87	44	0.83	748	6.08	
PENTANE	600	65	3	0.06	29	0.24	
PENTANOL	*	39	1771	33.42	728	5.92	PENTYL ALCOHOL
PENTANONE,2-	200	76	365	6.89	227	1.85	METHYL PROPYL KETONE

COMPOUND	T-12 COLUMN				G-24 COLUMN		SYNONYM
	TWA ppm	RR %	tR' sec	a	tR' sec	a	
PENTANONE,3-	200	61	355	6.70	257	2.09	DIETHYL KETONE
PROPANE	1000	70	1	0.02	5	0.04	
PROPANOL	200	35	351	6.62	102	0.83	PROPYL ALCOHOL
PROPANOL,2-	400	60	153	2.89	57	0.46	ISOPROPANOL
PROPYL ACETATE	200	60	283	5.34	286	2.33	
PROPYL ETHER	*	56	36	0.68	217	1.76	
PROPYL FORMATE	*	58	157	2.96	111	0.90	
PROPYLENE	*	36	2	0.04	4	0.03	
PROPYLENE OXIDE	20	66	46	0.87	40	0.33	1,2-EPOXYPROPANE
PYRIDINE	5	109	—	0.00	—	0.00	
STYRENE	50	92	1384	26.11	1355	11.02	
TETRACHLOROETHANE,1,1,1,2	*	81	956	18.04	810	6.59	
TETRACHLOROETHYLENE	25	67	141	2.66	603	4.90	PERCHLOROETHYLENE
TETRAHYDROFURAN	200	47	106	2.00	125	1.02	
TOLUENE	100	126	262	4.94	391	3.18	METHYL BENZENE
TRICHLOROETHANE,1,1,1-	350	101	53	1.00	123	1.00	METHYL CHLOROFORM
TRICHLOROETHANE,1,1,2-	10	95	1158	21.85	378	3.07	
TRICHLOROETHYLENE	50	54	104	1.96	222	1.80	
TRIETHYLAMINE	10	59	—	0.00	34	0.28	
TRIMETHYLPENTANE,2,2,4-	*	91	14	0.26	221	1.80	ISOOCTANE
VINYL ACETATE	10	40	116	2.19	77	0.63	
VINYL CHLORIDE	1	38	5	0.09	9	0.07	
XYLENE,m-	100	107	563	10.62	1135	9.23	1,3-DIMETHYL BENZENE
XYLENE,o-	100	106	804	15.17	1366	11.11	1,2-DIMETHYL BENZENE
XYLENE,p-	100	106	545	10.28	1140	9.27	1,4-DIMETHYL BENZENE

KEY:

* No TWA levels available.

TWA 8 Hour Time Weighted Average for
Maximum allowable exposure.

RR Relative Response to METHANE in Percent =
(Measured Response / Prepared Concentration) x 100.

— tR data not available

tR = Solute Retention Time from point of injection

tR' = Adjusted Retention Time in seconds

tM = Gas Hold-Up, or Dead Time

tR' = tR - tM

a = Relative Retention as compared to a Reference
Reference Compound is 1,1,1-Trichloroethane

Data collected at a chart speed = 1 cm/min. at
concentrations of 50 or 100 ppm, and at ambient
temperature

HOW TO USE THIS CHART FOR IDENTIFICATION OF UNKNOWNNS BY GC

1. Calculate the Adjusted Retention time of the Unknown solutes and of the Reference compound for the selected column. This can be accomplished by either running the reference compound separately, under similar conditions as the unknown will be run, or along with the questioned sample by introducing it into the sample stream via direct injection, dilutor accessory, or other like means. The t_R' for any solute is equal to the time elapsed from the point of injection to the projection of the peak maximum, minus the gas hold-up time of the column. The gas hold-up time is the time elapsed from the point of injection to the maximum deflection of the air peak. (NOTE: approximate hold-up times are 5 secs for a T-12 column and 10 secs for a G-24 column.)
2. In order to minimize the effects of minor variation in operating conditions and in the stationary phase loading of the columns, the parameter of Relative Retention (α) is used. To calculate α , for a particular solute on a given column, divide the t_R' of the solute by the t_R' of the reference compound. If the value of α falls within $\pm 10\%$ of the chart value, then the chances are good that the questioned solute is one of the compounds in this range.
3. To increase the probability of identifying an unknown solute, this chart provides the user with the option of Two-Column dimensional chromatography. By utilizing a second type column, one can calculate a second α value for the questioned solute. If this value of α falls within $\pm 10\%$ of the chart value, and the value of α for the previous column falls within $\pm 10\%$ of that chart value, then there is a high probability that the unknown has been identified.
4. Laboratory GC analysis and standard preparation may be required for confirmation, depending upon the application.

EXERCISE #5

Detector Tubes

OBJECTIVE

During this exercise, participants will learn how to do a leak check and a volume check of both a Draeger and a Sensidyne detector tube pump and how to use detector tubes quantitatively and qualitatively.

INTRODUCTION

There are chemical indicators that use the reaction of a chemical reagent with the airborne chemical of interest to produce a color change. The intensity of the color change or the length of color change is used to determine the amount of airborne chemical present. The chemical reagent may be impregnated on a piece of paper or tape and the color change read by eye or by an electronic device. The chemical could also be placed in a glass tube called a colorimetric indicator tube or detector tube.

PRINCIPLE OF OPERATION

Colorimetric indicator tubes or detector tubes (**Figure 1**) consist of glass tube impregnated with an indicating chemical. A known volume of contaminated air passes through or into the tube. The contaminant reacts with the indicator chemical in the tube, producing a change in color whose length or intensity is proportional to the contaminant concentration.

The tubes may have a preconditioning filter preceding the indicating chemical to:

- Remove contaminants (other than the one in question) that may interfere with the measurement. Many have a prefilter for removing humidity.
- React with a contaminant to change it into a compound that reacts with the indicating chemical.

TYPES OF TUBES

Detector tubes can be classified by the way air is drawn into the tube:

- Short-term tubes use a hand pump to draw air through the tube for a sample duration of a few seconds to a few minutes. This is used to give an instantaneous sample. The hand pump may be a **piston** or **bellows** type pump. This exercise will use both types. A piston pump has a handle that is pulled to evacuate a cylinder of known volume. Air is pulled through the tube to equalize the pressure in the cylinder.

MSA, Sensidyne, Enmet, and Matheson manufacture piston pumps. In a bellows pump, the bellows is squeezed and released. Air is pulled through the tube as the bellows expands. Draeger and MSA manufacture bellows-type pumps.

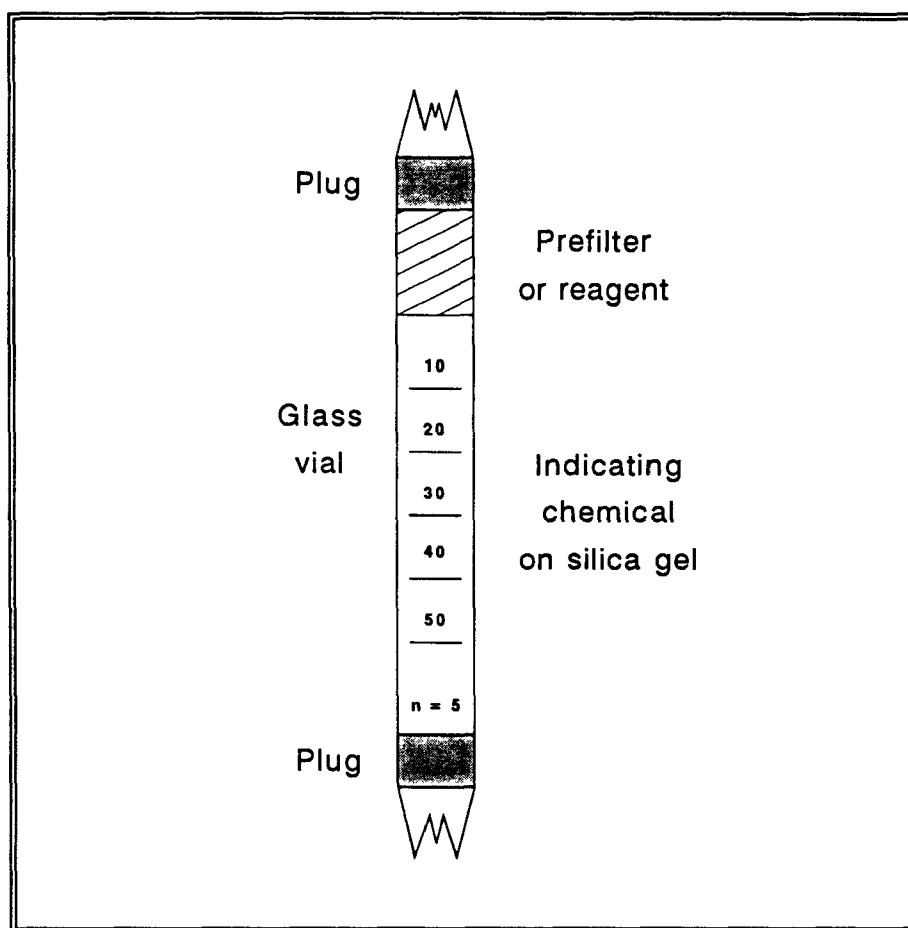


FIGURE 1. DETECTOR TUBE EXAMPLE

- Long-term tubes (pump) use a battery-operated pump to draw air through the tube over a longer period of time, usually 8 hours. These are used to determine 8-hour, time-weighted average exposures.
- Long-term tubes (dosimeter) do not use a pump. Contaminants diffuse into the tube over a long period of time, usually 8 hours. These also are used for 8-hour, time-weighted average exposure determination. However, a pump is not required for operation.

The three types of tubes are not interchangeable. They are calibrated for their specific applications. There are many more short-term tubes than there are long-term tubes.

Detector tubes can also be classified by the information generated the results:

- **Chemical groups**—Some tubes will react to a class of chemicals (e.g., alcohols or hydrocarbons). They will only indicate that a chemical of a certain class is present.
- **Specific chemicals**—There are a few tubes that only react to that specific chemical. Most tubes have a specific chemical listed for the tube, but can react to other chemicals (interferences).
- **Concentration ranges**—There may also be different concentration ranges for the same chemical. For example, there are tubes for carbon monoxide with concentration ranges of 5–150 ppm, 10–300 ppm, 0.1–1.2% and 0.3–7%.

DETECTOR TUBE CONSIDERATIONS

There are several factors that determine the effective use of detector tubes. These factors can be found in the instructions issued with each box of tubes.

Chemical Group: Some tubes are for a specific chemical and some are for a group of chemicals.

Lot #: The instructions for the tubes may change with different model numbers or different lots. Thus, the instructions should be matched with the proper tubes.

Expiration Date: The chemicals used in the tubes deteriorate over time. Because of this, the tubes are assigned a shelf life and the expiration date is printed on the box. This varies from 1 to 3 years.

Pump Strokes/Volume/Time: The total volume of air to be drawn through the tube varies with the type of tube. The volume needed is given as the number of pump strokes needed, i.e., the number of times the piston or bellows is manipulated. Also, the air does not instantaneously go through the tube. It may take 1 to 2 minutes for each volume (stroke) to be completely drawn. Therefore, sampling times can vary from 1 to 30 minutes per tube. This can make the use of detector tubes time consuming.

Color Change: The instructions will give the appropriate color change for indicating the chemical of concern. Other color changes may be noted for interferences. This information can be used to check for the presence of other chemicals.

Interferences: As mentioned previously, not every tube is specific. For example, an acetone tube will also respond to other ketones. Thus, methyl ethyl ketone would be considered an interference if one were checking for acetone. The instructions will give known interferences or color changes that are not for the chemical of interest.

Temperature/Humidity/Pressure: The length of color change (stain) can be affected by temperature, humidity and barometric pressure. If this is a problem, the instructions will note it and may give correction factors. Cold weather slows the chemical reaction in the tube and reduces the reading. Hot temperatures increase the reaction and can cause a problem by discoloring the indicator even

when a contaminant is not present. This can happen even in unopened tubes. Therefore, the tubes should be stored at a moderate temperature or even be refrigerated during storage.

Reusable?: Most tubes can only be used once, even if there is a negative result. There are some tubes, however, that can be reused the same day until a positive result is obtained.

Accuracy: The accuracy of detector tubes vary. Some studies have reported error factors of 50% and higher for some uncertified tubes. Some tubes are certified to be $\pm 25\%$ accurate at readings from 1 to 5 times the OSHA Permissible Exposure Limit (PEL) and $\pm 35\%$ at concentrations one-half the PEL. Only a few tubes are presently certified. Certification of detector tubes is being done by a private organization - Safety Equipment Institute (SEI).

One factor that affects accuracy is the interpretation of the end of the color change. Some color changes are diffused and the endpoint is not definite; others may have an uneven endpoint (**Figure 2**). When in doubt, use the highest value that would be obtained from reading the different aspects of the tube.

APPLICATIONS

Although there are many limitations and considerations for using detector tubes, detector tubes allow the versatility of being able to measure a wide range of chemicals with a single pump. Also, there are some chemicals for which detector tubes are the only direct-reading indicators.

They can be used to get a reading for a specific chemical in an atmosphere where a total vapor survey instrument would response to all the chemicals in the atmosphere. They also give an immediate response. Laboratory analysis (see the *Air Sample Collection* section) that can identify and quantify a chemical in a mixture takes time.

Manufacturers use general tubes for identification in their HazMat kits. These kits identify or classify the contaminants as a member of a chemical group such as acid gas, halogenated hydrocarbon, etc. This is done by sampling with certain combinations of tubes at the same time by using a special multiple tube holder or by using tubes in a specific sampling sequence. All manufacturers of detector tubes have some kind of system for hazard categorization. Detector tube manufacturers are listed in the *Manufacturers and Suppliers of Air Monitoring Equipment* section of this manual.

SAFETY

Do not directly inhale the contents of the bags and keep the bags closed when not in use. The contents of the gas bags, if released into the room, will not pose a hazard to the occupants.

Breaking the tips off the detector tubes can create a hazard. Please ensure that the glass tips are discarded into the containers provided and not onto the table or floor. The tube breakers built into the pumps can propel bits of glass. Direct the glass into the container provided. The instructor will demonstrate proper procedures. The ends of the detector tubes are also sharp, so handle them carefully.

Eating or drinking is not allowed during this exercise because it is nearly impossible to prevent small shards of glass from being deposited on the desk, table, or floor. Also, check the work area so that you do not pick up glass on your hands or arms.

PUMP CHECK - DRAEGER

Leak Test

The purpose of this test is to ensure that air is going through the tube and not around it or through a leaky valve.

1. Insert an unopened tube into the socket of the pump. Do not use your finger to seal the orifice. The instructor will demonstrate why not.
2. Squeeze the pump completely and release. If the indicator mark has not appeared in 15 minutes, the pump passes the test. You may want to go to the Sensidyne pump check while this is taking place.
3. If the pump fails the test, inform the instructor.
4. Remove tube from the socket.
5. (New model pump) Press counter reset button with a ball point pen or end of unopened tube to set at zero.

Volume Check

The purpose of this step is make sure that the pump is drawing the specified volume (100 cubic centimeters or milliliters). The tubes are calibrated for this volume. If the volume is not within limits, the tubes can not be used quantitatively.

6. Break off the tips of a tube or use a previously opened tube.
7. Connect the detector tube and pump to the apparatus as shown in **Figure 2**.

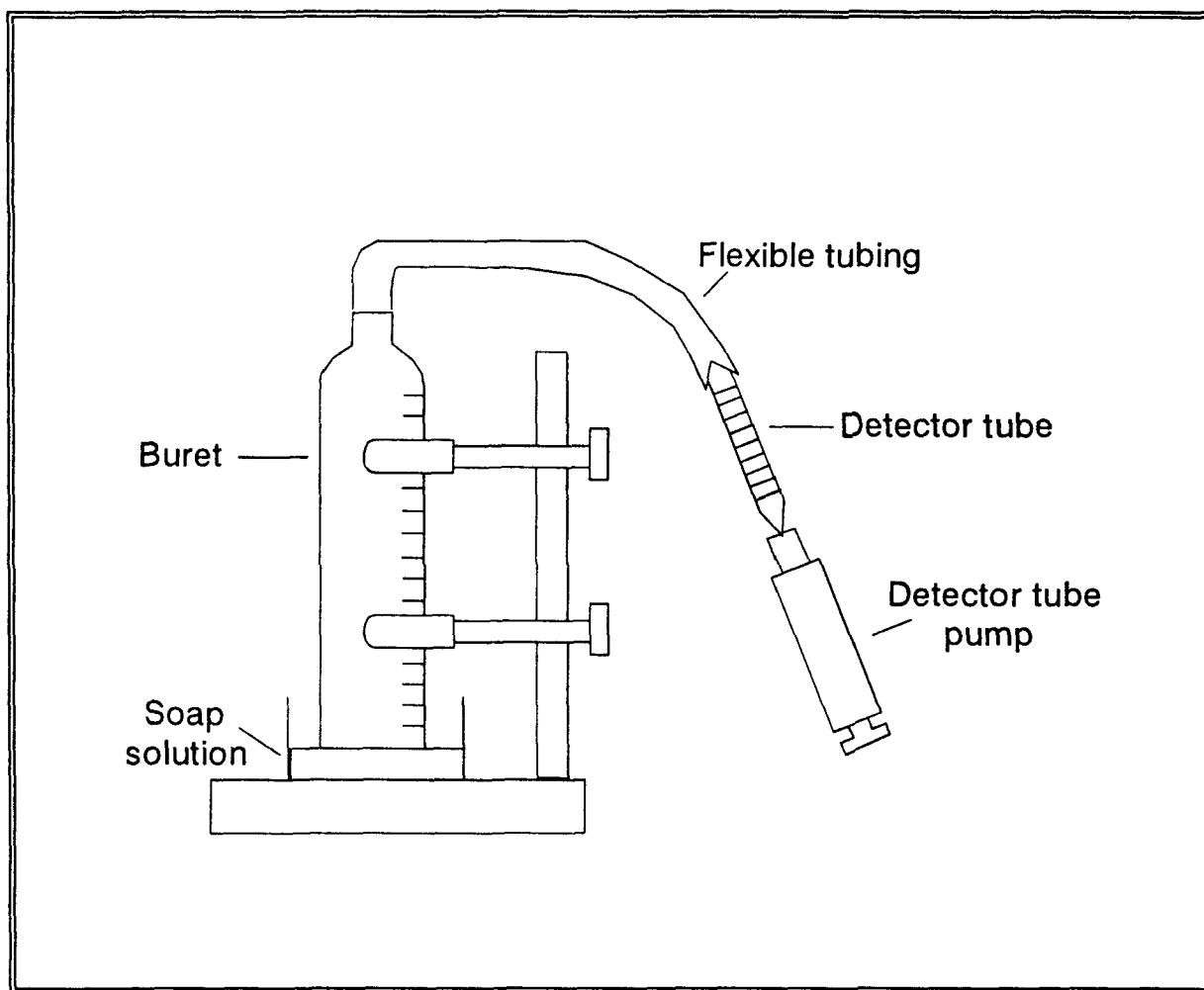


FIGURE 2. DETECTOR TUBE PUMP VOLUME CHECK APPARATUS

8. Start a bubble at the mouth of the inverted buret by just touching the soap solution to the mouth of the buret.
9. Squeeze the bellows pump in order to pull the bubble up the buret. Continue to squeeze and release the pump until the bubble stops above the "0" mark on the buret. This maneuver may require disconnecting the flexible tubing after the bubble passes the "0" mark.
10. Start with the bellows fully expanded. Reconnect the detector tube to the tubing. Record the start point (ml) in **Table 1**.
11. Squeeze and release the pump.
12. When the bubble stops, record the stopping point (ml).
13. The difference in the two points (the travel volume) is the volume pulled by one stroke of that pump. This volume should be between 95 and 105 ml ($100 \text{ ml} \pm 5\%$).
14. You may repeat the test to see whether the results are consistent.

PUMP CHECK - SENSIDYNE

Leak Test

1. Insert an unbroken tube into the orifice of the pump.
2. Align the index marks on the pump handle and the pump cap. Pull the handle straight out as far as it will go. It should lock in place.
3. Wait 1 minute. Turn the handle 1/4 turn and release the handle. Hold the pump barrel firmly as the handle will pop back rapidly if the pump does not leak. The handle should return to within 1/4 inch of the cap. If the pump is equipped with a "Flow Finish Indicator," the red button will remain down if there is no leak.
4. If the pump fails the test, inform the instructor.

Volume Check

5. Break off the tips of a tube or use a previously opened tube.
6. Connect the detector tube and pump to the apparatus as shown in **Figure 2**. An adapter may be needed because of the small diameter of the tube.
7. Start a bubble at the mouth of the inverted buret by just touching the soap solution to the mouth of the buret.
8. Pull the handle back in order to pull the bubble up the buret. Continue to pull the handle until the bubble stops above the "0" mark on the buret. This maneuver may require disconnecting the flexible tubing after the bubble passes the "0" mark.
9. Start with the piston empty (handle fully in). Reconnect the detector tube to the tubing. Record the start point (ml) in **Table 1**.
10. Pull back the pump handle all the way.
11. When the bubble stops, stop the stopwatch. Record the time and the stopping point (ml).
12. The difference in the two points (the travel volume) is the volume pulled by one stroke of that pump. This volume should be between 95 and 105 ml ($100 \text{ ml} \pm 5\%$).
13. You may repeat the test to see if the results are consistent.

QUANTITATIVE RESULTS - DRAEGER AND SENSIDYNE

The pumps and detector tubes will be used to determine the concentration of two chemicals. The Draeger pump and tube will be used to determine the concentration of carbon dioxide in the gas bag. The Sensidyne pump and tube will be used to determine the concentration of isopropyl alcohol in the air above a beaker of liquid.

1. Read the instructions for the detector tube.
2. Determine the number of pump strokes needed; the color change expected; and any adjustments to the reading.
3. Use a fresh tube. Break off both ends of the tube. Insert the opened tube into the pump orifice with the arrow on the tube pointing towards the pump. Sample the bag (carbon dioxide) and the air above the liquid (isopropyl alcohol). Do not pull liquid into the tube. (This is air, not water, monitoring.) Liquid drawn into the tube can produce a change even if the chemical is not present.
4. Record your results on **Table 1**.

CHEMICAL CLASSIFICATION - DRAEGER

In this step, a series of Draeger tubes will be used to determine the types of chemicals in an unknown mixture. The flow chart on the next page will be used to determine the mixture's components. The chart was provided by National Draeger, Inc. Other manufacturers have similar systems for chemical classification.

This sample taking schedule refers to a selection of substances which occur frequently in practice. Other situations may necessitate another sequence of measurements and, the case being, the use of additional detector tubes, or measurements according to other procedures must be carried out. (from National Draeger, Inc.)

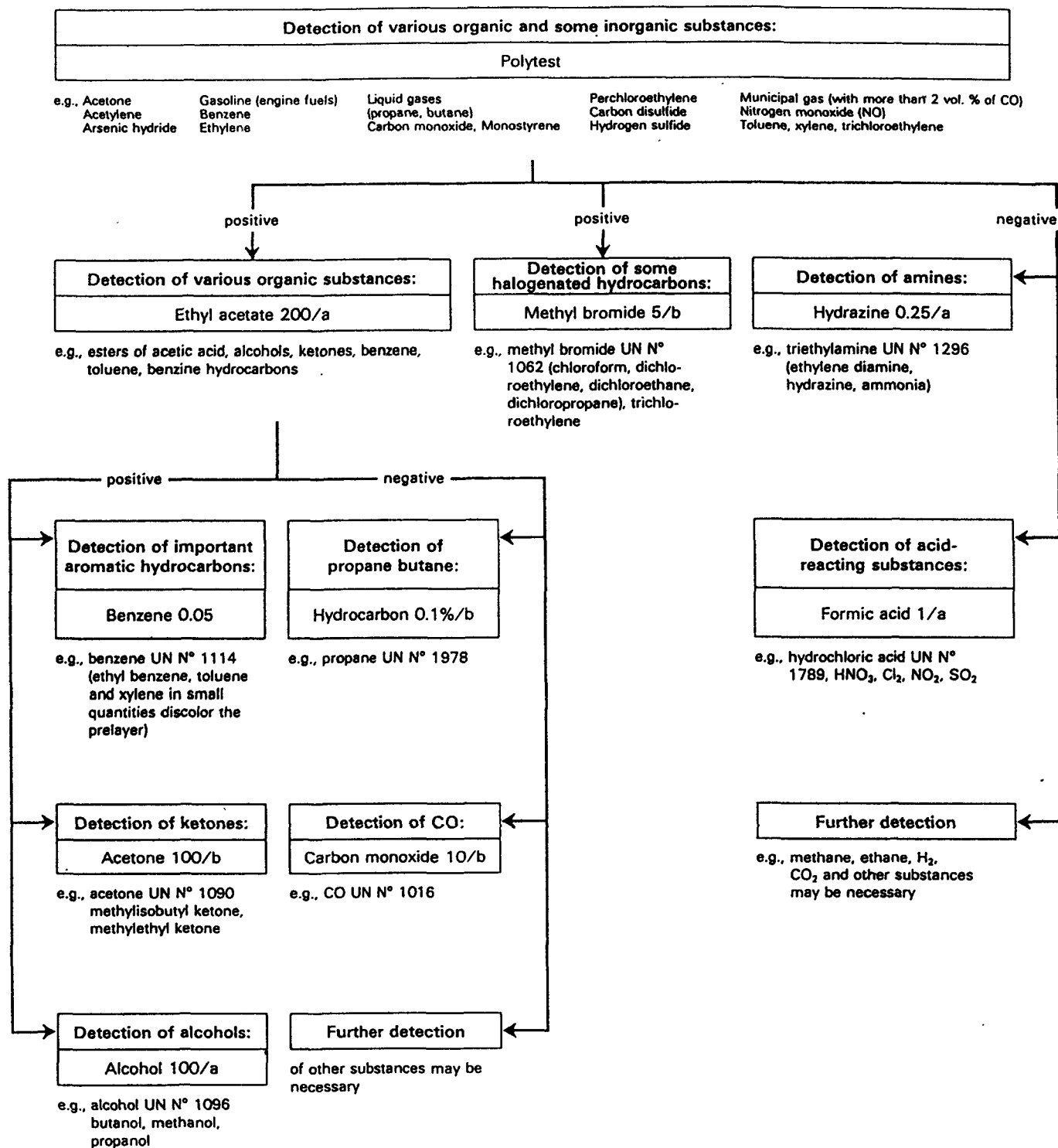
The information on the next two pages has been reprinted with the permission of National Draeger, Inc., Pittsburgh, PA. This information can also be found in their Haz Mat Kit. Similar flow charts/decision logics have also been developed by MSA and Sensidyne for use with their detector tubes.

1. Read the instructions for the tubes.
2. Use the tubes to sample the unknown atmosphere.
3. Record the result in the appropriate space in **Table 2**.
4. Repeat process with all the tubes provided.
5. Extra space is provided should any special tubes be used.

Safety Tips

The POLYTEST and HYDROCARBON tubes use sulfuric acid as a reagent. When the bellows is squeezed, an aerosol (smoke-like) containing the acid will be emitted. Avoid breathing the "smoke." If you think you may have some problems with the aerosol, please inform your instructor. You should not have any problems unless you are more sensitive than the average person.

Detection of unknown substances by means of DRAEGER detector tubes*



*Important: This sample taking schedule refers to a selection of substances which occur frequently in practice. Other situations may necessitate another sequence of measurements and, the case being, the use of additional detector tubes, or measurements according to other procedures must be carried out.



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Examples for the (qualitative) indication response of the DRAEGER Polytest tubes

The results were obtained under the following test conditions:

Temperature 20°C; Humidity 50% relative; All tests carried out with pure substances

Substance	Concentration	Number of strokes of the bellows pump	Length of Discoloration	Notes on the indication
Acetone	5000 ppm	5	approx. 10 mm	brownish green
Acetone	above liquid	5	completely colored	brownish
Acetylene	200 ppm	5	approx. 10 mm	brownish green
Acetylene	high conc. (over 1 %)	5	completely colored	brownish
Arsine	10 ppm	5	approx. 10 mm	brownish green
Arsine	high conc. (over 1 %)	5	completely colored	brownish
Benzine (Gasoline)	50 ppm	5	approx. 10 mm	brownish green
Benzine (Gasoline)	above liquid	5	completely colored	brownish
Benzene	100 ppm	5	approx. 10 mm	brownish
Benzene	above liquid	5	approx. 10 mm	brownish
Butane	100 ppm	5	approx. 10 mm	faded green (spotty)
Butane	high conc. (over 1 %)	5	completely colored	brownish green
Carbon disulfide	10 ppm	5	approx. 10 mm	greenish
Carbon disulfide	above liquid	5	completely colored	brownish green
Carbon monoxide	100 ppm	5	approx. 10 mm	brownish green
Carbon monoxide	high conc. (over 1 %)	5	completely colored	brownish
Ethylene (ethene)	500 ppm	5	approx. 10 mm	brownish green
Ethylene (ethene)	high conc. (over 1 %)	5	completely colored	brownish
Nitrogen monoxide (NO)	50 ppm	5	approx. 10 mm	brownish green
Nitrogen monoxide (NO)	high conc. (over 1 %)	5	completely colored	brownish with bleaching effect
Perchloroethylene	50 ppm	5	approx. 10 mm	greenish
Perchloroethylene	above liquid	5	completely colored	brownish green
Propane	500 ppm	5	approx. 10 mm	faded green (spotty)
Propane	high conc. (over 1 %)	5	completely colored	brownish green
Styrene (monostyrene)	500 ppm	5	approx. 10 mm	brownish
Styrene (monostyrene)	above liquid	5	approx. 10 mm	brownish
Toluene	200 ppm	5	approx. 10 mm	brownish
Toluene	above liquid	5	approx. 10 mm	brownish
Trichloroethylene	50 ppm	5	approx. 10 mm	brownish green
Trichloroethylene	above liquid	5	completely colored	faded yellow
Xylene	500 ppm	5	approx. 10 mm	brownish
Xylene	above liquid	5	approx. 10 mm	brownish

Examples for the (qualitative) indication response of the DRAEGER tubes for ethyl acetate 200/a

The results were obtained under the following test conditions:

Temperature 20°C; Humidity 50% relative; All tests carried out with pure substances

Substance	Concentration	Number of strokes of the bellows pump	Length of Discoloration	Notes on the indication
Acetone	3000 ppm	5	approx. 10 mm	greenish
Acetone	above liquid	5	completely colored	greenish
Benzene	500 ppm	5	completely colored	very pale grey
Benzene	above liquid	5	completely colored	greenish grey
Ethyl alcohol	2000 ppm	5	approx. 5 mm	greenish
Ethyl alcohol	above liquid	5	approx. 20 mm	greenish
Octane	100 ppm	5	approx. 10 mm	grey-brown-greenish
Octane	above liquid	5	completely colored	greenish
Toluene	500 ppm	5	approx. 10 mm	greenish grey
Toluene	above liquid	5	completely colored	greenish grey
Xylene	500 ppm	5	approx. 10 mm	greenish brown
Xylene	above liquid	5	completely colored	greenish brown



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TABLE 1		
	SENSIDYNE	DRAEGER
ID NUMBER		
LEAK CHECK	PASS FAIL	PASS FAIL
VOLUME CHECK		
BURET STOP POINT (ml)		
BURET START POINT (ml)		
TOTAL VOLUME		
SAMPLE TIME		
ACCEPTABLE VOLUME? ^a	PASS FAIL	PASS FAIL
SAMPLES	<i>ISOPROPYL ALCOHOL</i>	<i>CARBON DIOXIDE</i>
UNADJUSTED READING		
READING ADJUSTED FOR TEMPERATURE		
READING ADJUSTED FOR BAROMETRIC PRESSURE ^b		

- ^a The acceptable volume for a full pump stroke is 100 ml \pm 5% (i.e., between 95 and 105 ml).
^b Assume the sampling conditions were 30°C and 720 mm barometric pressure.

TABLE 2	
NAME OF TUBE	READING/INDICATION
POLYTEST	
METHYL BROMIDE	
ETHYL ACETATE	
BENZENE	
ACETONE	
ALCOHOL	
HYDROCARBON	
CARBON MONOXIDE	
HYDRAZINE	
FORMIC ACID	

What types of chemicals are present in the mixture?

QUESTIONS

1. Based on your test results, how long should you wait between pump strokes for the MSA?
2. What factors could affect the detector tube results?
3. Does the CO₂ concentration exceed the PEL? REL? TLV? IDLH?
4. Does the isopropyl alcohol concentration exceed the PEL? REL? TLV? IDLH?

EXERCISE #6

Direct-Reading Aerosol Monitors

OBJECTIVE

Participants will learn how to operate the MIE Real-Time Aerosol Monitor Model RAM-1 and the MIE MINIRAM Personal Monitor Model PDM-3.

DESCRIPTION OF EQUIPMENT

The RAM-1 and the MINIRAM are portable, self-contained aerosol monitors. Their detection system is based on the detection of near-forward, scattered, near-infrared radiation.

The RAM-1 uses a pump to draw air into the unit to the sensors. It uses an air screen to prevent contamination of the sensors. The MINIRAM does not require a pump. Air passes through the sensing volume by convection, circulation, ventilation and personnel motion. The sensors are also in direct contact with the environment. Thus, there is a chance the sensors may get covered with dust. The MINIRAM sensors require cleaning on a regular basis.

Both units indicate the aerosol concentration in milligrams per cubic meter (mg/m^3). Both use a digital display. The MINIRAM's displayed reading is updated every 10 seconds. The RAM-1 has a variable time display.

The RAM-1 has a range of 0.000–200.0 mg/m^3 . The readout range is selected by the operator. The MINIRAM normally operates in the 0.00 to 9.99 mg/m^3 range. Whenever a 10-second concentration exceeds 9.99 mg/m^3 , the MINIRAM automatically switches to the 0.0 to 99.9 mg/m^3 range and remains in that range as long as the measured 10-second concentration exceeds 9.99 mg/m^3 . Otherwise the MINIRAM reverts to its lower range display.

The RAM-1 only displays real-time concentrations. A output device can be connected to record data. The MINIRAM can store data for later output and for TWA calculations. Thus, it can be used as a direct-reading monitor and a dosimeter.

Both instruments can be powered by internal batteries or an external AC source.

It is important to remember that these instrument only give total or respirable quantities of aerosols. They do not give the composition of the aerosol. To determine the composition of the aerosol, a sample must be taken and analyzed. Refer to the *Air Sample Collection* section of the course manual.

MIE MINIRAM PERSONAL MONITOR MODEL PDM-3

Before using the instrument without the charger, charge the MINIRAM for a minimum of 8 hours.

Initial Condition

- Blank display—Indicates that the MINIRAM has not been in the measurement mode for 48 hours or more, and is in the minimum power off mode.
- "OFF" display—MINIRAM has been in the off mode for less than 48 hours.
- Concentration display that changes or "blinks" once every 10 seconds: the MINIRAM is in the measurement mode.

Controls (refer to Figure 1)

"MEAS" When this button is pressed, the measurement mode will start. Once the MEAS mode has been entered, this sequence can only be interrupted by pressing OFF. Pressing ZERO, TWA, SA, TIME, or ID# only affects the display during the time the keys are pressed.

The readout will first display "GO" (or "CGO" if TIME is also pressed) followed by the last concentration reading or ".00."

Approximately 36 seconds later, the first new 10-second-averaged concentration reading is displayed. The reading will be updated and displayed every 10 seconds.

The MINIRAM will now run in the measurement mode for 500 minutes (8 hours and 20 minutes), after which time it will stop, displaying the OFF reading. It will retain in storage the concentration average and elapsed time information.

If both MEAS and TIME are pressed at the same time (press TIME first and while depressing it actuate MEAS) the MINIRAM will display "CGO," and will then operate as above (i.e., pressing MEAS only), except that after the first 8.3-hour run, it will restart automatically and continue to measure for an indefinite number of 8.3-hour runs, (with the battery charger) until the OFF key is pressed, or until the batteries are exhausted. Concentration averages and timing information for the last seven 8.3-hour runs will remain in storage at any give time.

"ZERO" When instrument displays "OFF," pressing this button initiates the ZERO procedure.

"TIME" During the measurement mode, if TIME is pressed, the display will show the elapsed time, in minutes, from the start to the last measurement run. The MINIRAM will automatically return to concentration display after the TIME key is released.

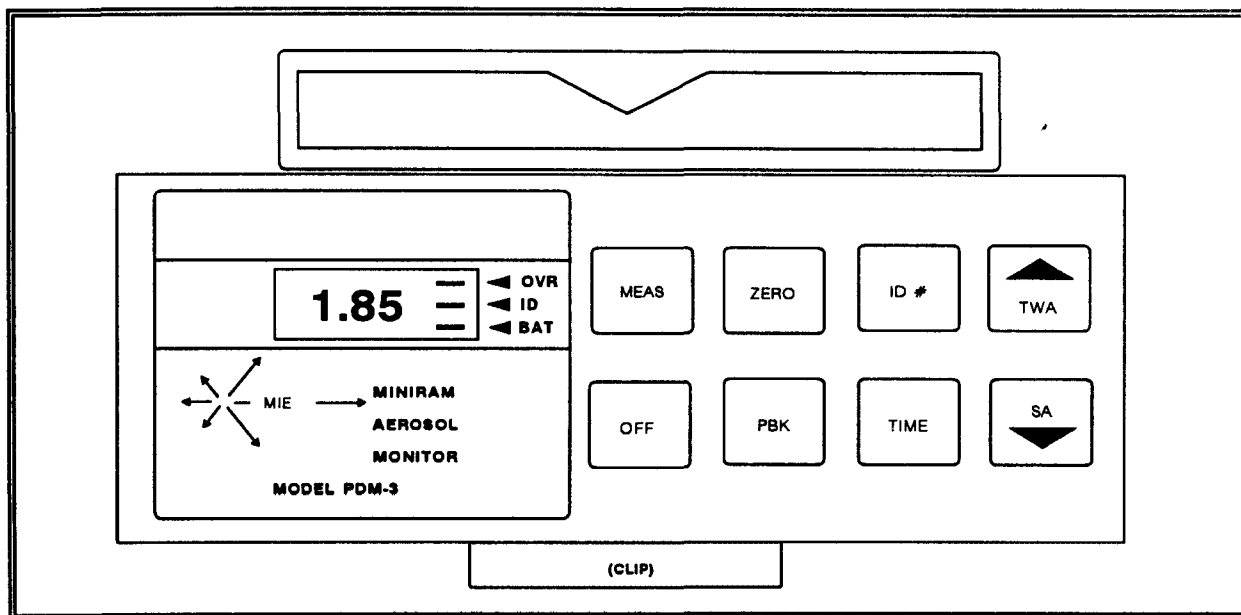


FIGURE 1. FRONT PANEL OF MINIRAM

- "TWA"** During the measurement mode, if the time-weighted average (TWA) is pressed, the display will indicate the average concentration in milligrams per cubic meter (mg/m^3) up to that instant, from the start of the last run. The value of TWA is updated every 10 seconds. After releasing the TWA key, the MINIRAM display returns to the 10-second concentration display.
- "SA"** During the measurement mode, pressing SA (Shift-Average) will provide a display of the aerosol concentration, up to that moment, averaged over an 8-hour shift period.
- "PBK"** With the MINIRAM in the off mode, the stored information can be played back by pressing PBK (Play Back). Pressing the PBK key for more than 1 second will cause stored data to be automatically played back through the MINIRAM display: First, the identification number is displayed with the ID indicator bar on; next the shift or run number (i.e., 7 through 1, starting with the last run) is shown (with the OVR indicator bar on as identification); followed by the sampling time in minutes, for that run; followed by the off-time between the last and next run (in tens of minutes; finally, the average in mg/m^3 . This sequence is repeated seven times. An average reading of 9.99 indicates that a significant overload condition occurred during that run. The total time required for the complete automatic playback on the MINIRAM display is approximately 70 seconds.
- "OFF"** When this key is pressed, the MINIRAM will discontinue whatever mode is underway displaying "GCA" followed by the display segments check ("8.8.8=") and finally "OFF." The MINIRAM will then remain in this reduced power condition (displaying "OFF").

Display

During the measurement mode, the display indicates the present concentration in mg/m^3 . If one of the function buttons is pushed, the information indicated in **CONTROLS** is displayed. If a bar appears in the display, the bar's location indicates one or more of the following:

- | | |
|-------|---|
| "OVR" | The concentration exceeds the range of the instrument or there is an overload due to reflected line (e.g., sunlight). |
| "ID" | This indicates that the ID number is being displayed and not a concentration. |
| "BAT" | This indicates a low battery. |

Zero Procedure

1. Zeroing must be performed in a clean-air environment. This can be done by using a clean room or clean-bench, flowing clean air through the sensing chamber, or using an air-conditioned office (without smokers).
2. Press OFF and wait until the display indicates "OFF."
3. Depress the ZERO button. Wait until the display again indicates "OFF." The average of four consecutive 10-second zero level measurements will then be stored by the MINIRAM as the new ZERO reference value. The ZERO reference value will be subtracted from subsequent readings. When operating the MINIRAM in high particle concentration environments ($>5 \text{ mg}/\text{m}^3$) the zero value should be updated approximately every 8 hours. At aerosol concentrations below approximately $1 \text{ mg}/\text{m}^3$ this update may only be required once a week.

Start Measurement Cycle

4. Place the MINIRAM in the area to be monitored. The instrument should be placed vertically (i.e., display/control panel facing upwards) by clipping it to a belt, shoulder strap, etc.
5. If the MINIRAM shows a blanked display, press OFF and wait until the display reads "OFF" (approximately 5 seconds after pressing OFF) before pressing MEAS to initiate measurement cycle.
6. If the MINIRAM shows "OFF," press MEAS directly to initiate measurement cycle (there is no need to press OFF first, in this case).
7. Press MEAS.
8. Observe the readings for 1 minute to verify that the levels change every 10 seconds and that the OVR bar is not displayed.

9. Avoid objects being placed in the sensing chamber. Also avoid direct sunlight scattering in the sensing chamber.
10. At the end of the sampling period, press "TIME." Record the sample duration in **Table 1**.
11. Press the TWA button. Record the reading in **Table 1**.
12. Press OFF.

TABLE 1	
INFORMATION	RESULTS
INSTRUMENT SERIAL #	
START TIME	
TWA	
SHIFT AVERAGE (SA)	
OFF TIME	

MIE REAL-TIME AEROSOL MONITOR MODEL RAM-1

In the following procedure, the numbered buttons, displays, and switches refer to the illustration of the RAM-1 in **Figures 2 and 3**.

Startup

1. Lift up protective cover of control panel.
2. Place selector switch (1) in battery (BATT) position.
3. Place inlet valve (2) in CLEAR position (horizontal).
4. Replace sealed cap on inlet valve with the restrictor orifice.
5. Switch instrument on (3) and check battery voltage. The digital readout (4) should indicate between 6.0 and 6.6 volts. If not, inform the instructor. The reading should be identified by a display of VDC (volts DC). Low battery voltage is indicated by a flashing "VDC" on the right-hand side of the display, whenever the selector switch is not in the BAT position.

Zeroing

6. Check that the inlet valve is in the CLEAR position (horizontal). Place the selector switch in the 0-200 position. The letter "m" should appear to the right of the display reading, indicating that the instrument is set to read concentration measurements.
7. Place the time constant switch (5) in the 2-second position.
8. Allow 1 minute for instrument to stabilize (warm-up). **IMPORTANT!**
9. If necessary, lift the cover over the ZERO control (6) and adjust the control until a reading of 00.0 is obtained.
10. Switch the selector to the 0-20 position and repeat step #9.
11. Switch the selector to the 0-2 position and repeat step #9. Readings may fluctuate. Try to obtain an average reading of 0 ± 0.005 .

Secondary Calibration

12. Keep inlet valve in its CLEAR position.
13. Set the range selector to the 0-20 position.
14. Unlock the hinged flow chamber cover and place in the horizontal position.

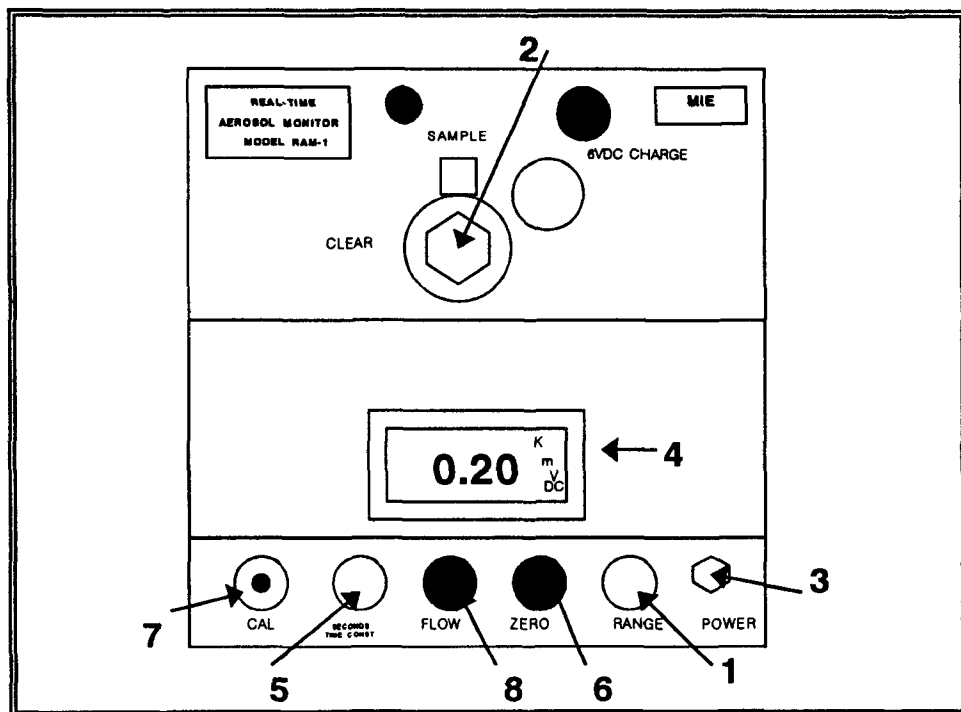


FIGURE 2. RAM-1 TOP VIEW

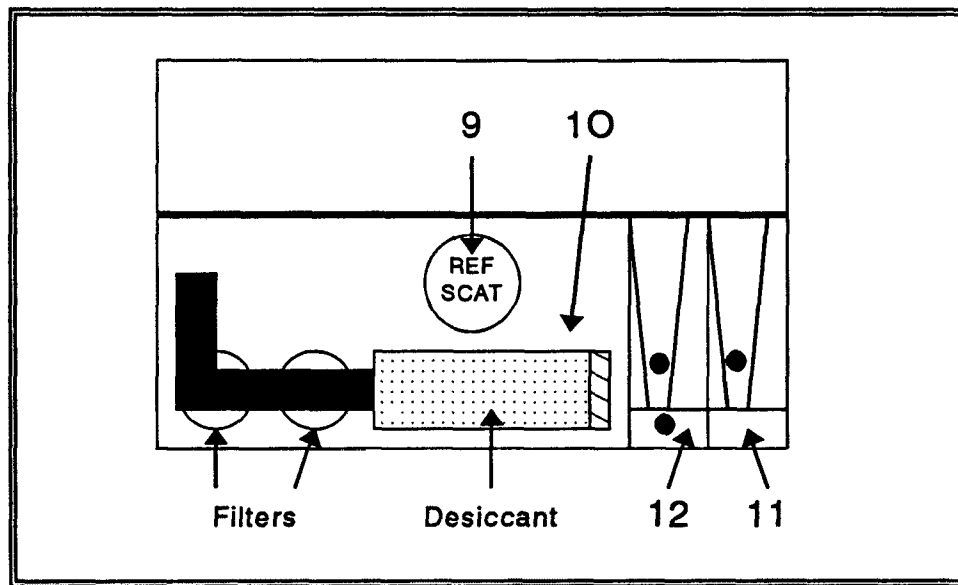


FIGURE 3. RAM-1 SIDE VIEW

15. Push the reference scatterer knob (REF SCAT) (9) inward until a positive stop is detected. The pump will automatically shut off. The letter "K" should be flashing in the upper right side of the display. Allow the reading to stabilize for 30 seconds.
16. See if the instrument reading corresponds with the factory calibration label (10) by the (REF SCAT).
17. If the indicated readings differ by more than 5%, adjust the CAL control (7) as required. The CAL control has a lock that must be disengaged before attempting to turn the knob. Allow to stabilize and repeat if required. Relock the CAL control.
18. Pull the REF SCAT back out.
19. Close the flow chamber cover and tighten thumb-screws.

Measurement Procedures

20. Switch RAM on.
21. Select measurement range (usually the 0-20 position).
22. Select desired time constant (usually 2 seconds).
23. Place inlet valve in SAMPLE position (vertical downwards).
24. Check the flow meters. The TOTAL (11) should read about 2 and the PURGE (12) should read about 0.2 (or 10% of TOTAL). Adjust the total flow rate with the flow adjust screw

- (8). Adjust the purge flow with the black valve on the rotameter. If the rotameter is pegged, check that the inlet valve is in the SAMPLE position.
25. Measure the aerosol concentrations in the areas designated by the instructor.
 26. If the aerosol concentration exceeds the maximum selected range, the RAM-1 will indicate 1 with all zeros blanked out. If this occurs, change the range selection to higher ranges as needed.
 27. Check and update zero periodically.
 28. **BEFORE SHUTTING OFF THE RAM-1, CLOSE THE INLET VALVE (CLEAR POSITION) AND OPERATE FOR 3 MINUTES TO ALLOW PURGING OF THE DUSTS INSIDE THE OPTICAL CAVITY.**
 29. When sampling and purging is complete, turn the instrument OFF.

-

EXERCISE #7

Gas Chromatography - PID

OBJECTIVE

The student will learn the basic operation of the Photovac 10S50 portable gas chromatograph and analyze several air samples.

PROCEDURE

The instructor will describe and illustrate the different parts of the Photovac 10S50 and their functions. Since the 10S50 needs a certain amount of warm-up time, the student will not be able to go through start-up of the instrument. After the introduction, students will run a calibration standard and an unknown sample. Students will also collect an air bag sample and analyze it.

OPERATING INSTRUCTIONS FOR THE PHOTOVAC 10S50 (CAPILLARY COLUMN OPERATION)

Preparation for Use

Refer to the Photovac 10S50 instrument panel and **Figure 1**.

Recharge the Carrier Gas

1. Connect the fill line for the Photovac 10S50 to a cylinder of "Ultra-Zero Air" (contents <0.1 ppm hydrocarbon).
2. Attach the "Quick-Connect" from the fill line to the REFILL receptacle on the upper right-hand corner of the Photovac 10S50.
3. Turn on the cylinder and rotate the valve for the fill line so that the pointed end points toward the cylinder. Be sure not to stand directly in front of the regulator.
4. The reservoir in the instrument will be filled to the maximum pressure of the supply cylinder. The pressure is indicated on the CONTENTS gauge on the upper left of the instrument panel. (The maximum pressure at which the instrument can be filled is 1750 psi.) The delivery pressure is indicated on the DELIVERY gauge. This pressure should be 40 psi. When the reservoir is filled, the excess air will be expelled at the fritted outlet on the supply cylinder regulator. This will be indicated by a "hissing" sound. Turn off the supply cylinder valve and then turn off the valve on the fill line.
5. Disconnect the fill line.

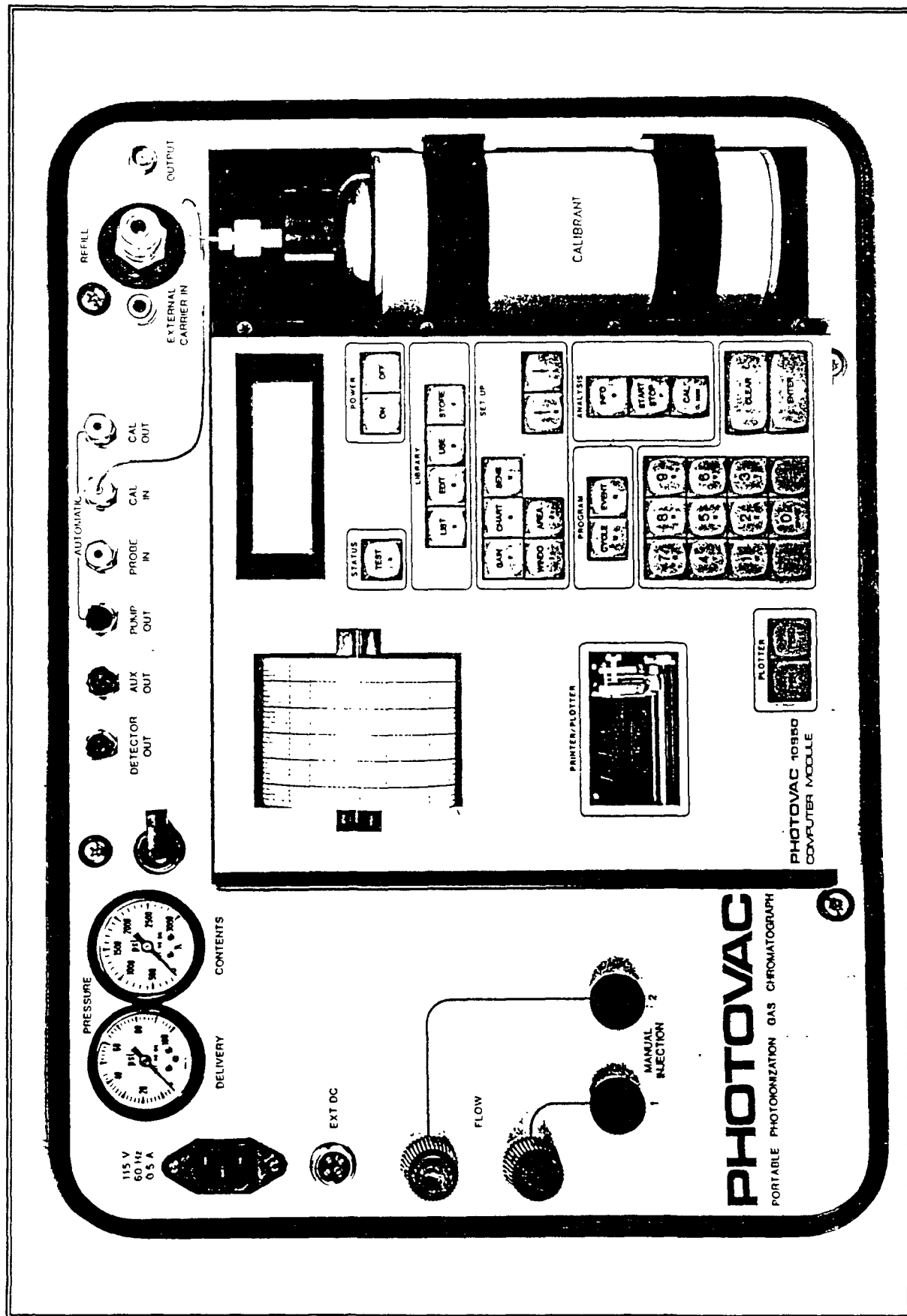


FIGURE 1. PHOTOVAC 10S50 INSTRUMENT PANEL
Source: *Photovac 10S50 Operating Manual*, Photovac Incorporated.

Set the Carrier Gas Flow Rate

6. The pieces of tubing to the flow meter are attached to the ports on the instrument panel.
7. Attach the line on the left side of the meter to the DETECTOR OUT port.
8. Attach the line on the right side of the meter to the needle valve marked AUX OUT.
9. Connections should be secured with a 7/16 inch open-ended wrench (1/4 turn past tight).
10. Adjust the flow rates on the meter.
 - a. If the instrument is being set up to stabilize overnight, set the DETECTOR OUT FLOW using the red FLOW adjustment knob on the left side of the panel to 5 ml/min. *Note:* Turn knob clockwise to decrease the flow or counterclockwise to increase the flow. Set AUX OUT flow using the needle valve to 0 ml/min. Allow to stabilize overnight.
 - b. If the instrument is being set up for analysis, set the DETECTOR OUT flow using the red FLOW adjustment knob to 10 ml/min. Set AUX OUT flow using the needle valve to 10 ml/min.

Activate the Power Source

11. When the instrument is ready for use, attach the power cord for the instrument to the 3-prong socket in the upper left-hand corner of the instrument. The cord is then plugged into an AC outlet.
12. Press the ON key. The instrument will respond with "LAMP NOT READY, PLEASE WAIT."
13. Wait until the display reads "READY ENTER COMMAND."

Set Instrument Parameters

14. Locate the LIBRARY block and press the USE key. The instrument will respond with "LIBRARY IN USE?" There are four libraries numbered 1 to 4. Library #1 is the default. We will use #1 for this exercise. Press the 1 key and then the ENTER key.
15. The instrument will prompt for "DAY" (1-31). Press the appropriate value for the day of the month and then press the ENTER key.

16. The following information is entered in the same manner:
 - a. MONTH (1-12), then press ENTER
 - b. YEAR (e.g., 1993), then press ENTER
 - c. HOUR (0-23), then press ENTER
 - d. MINUTE (0-59), then press ENTER.
17. The instrument will read: "READY ENTER COMMAND."

Obtain a Status Report

18. Locate the STATUS block and press the TEST key. The instrument will respond with "FUNCTION, USE < >, STATUS REPORT." Respond by pressing the ENTER key.
19. The instrument will print a status report containing the following information:
 - a. Current field date and time.
 - b. Field: The # represents the detector field in volts/10.
 - c. Power: The # indicates the current lamp consumption at mA/10.
 - d. EVENT settings show the ON and OFF times of the 10S50 sample pump and solenoid valves. The instructors will have set the following EVENT values:

SAMPLE	(EVENT #1)	0	10
CAL	(EVENT #2)	0	0
EVENT #3		10	60*
EVENT #4		0	10
EVENT #5		13	60*
EVENT #6		0	0
EVENT #7		0	0
EVENT #8		0	0

* Some units may have a longer time (e.g., 80) instead.

20. Allow the instrument to stabilize for approximately 45 minutes. The instrument has been stabilizing prior to the exercise so we may continue.

Select the Analytical Parameters

21. Locate the SETUP block on the instrument panel.

22. Press the GAIN key. The gain controls the amplification from the detector. The default value is "2" For higher values, press the UP ARROW key until the desired value appears. For this exercise, choose a gain setting of "5" and then press ENTER.
23. Press the CHART key. The instrument will respond with "CHART ON" or some other readout. "CHART ON" means the chromatogram will be displayed along with identification information and some instrument settings (e.g., GAIN). "CHART OFF" means that the chromatogram will not be displayed, but identification information and some instrument settings will be displayed. "CHART ON WITH BASELINE" prints out the same information as "CHART ON," but also shows the baseline the instrument uses to calculate peak area. "CHART ON WITH SETUP" prints out the same information as "CHART ON WITH BASELINE" but also includes the setup information (e.g., SENS, WINDO). Use the UP ARROW or DOWN ARROW key until "CHART ON WITH SETUP" is displayed. Press ENTER. The next display is the chart speed. The default is 0.1 cm/min. Press the UP ARROW key until 0.5 appears. Press ENTER.
24. Press the SENS key. The key controls the instrument integrator. The following settings specify the minimum response that will be recognized as a peak on the chromatogram.
- SLOPE UP; Use the arrow keys to display 18 mv. Then ENTER.
SLOPE DOWN; Use the arrow keys to display 16 mv. Then ENTER.
PW (Peak Width) at 4 minutes; Use the arrow keys to display 6 (sec). Then ENTER.
25. Press the WINDO key. This key adjusts the 10S50's tolerance to retention time drift. A peak must be within a specified percentage of a stored retention to be identified as that chemical by the instrument. Choose a value of "10" (i.e., 10%) and press ENTER.
26. Press the AREA key. This key sets a peak size threshold. All peaks smaller than the AREA setting are deleted from the "PEAK INFORMATION" listing at the end of the analysis. (However, these peaks will still be numbered on the chromatogram.) Set the minimum area at "50" and ENTER.
27. Locate the PROGRAM block and press the CYCLE key. The instrument will prompt for the following information:
- a. "TIMER DELAY." This setting determines the delay in time from when the START/STOP key is pressed and when the instrument will start looking for peaks. Choose "10" seconds and ENTER.
 - b. "ANALYSIS TIME." The duration of the analysis is dependent upon the types of compounds that are being considered for analysis. Select an analysis time of 600 seconds for this exercise. Press ENTER.
 - c. "CYCLE TIME." These times refer to the mode for continuous monitoring. This mode will not be used in this exercise. Choose "0" min and ENTER. The instrument will respond with "CYCLING DISABLED, COUNTERS RESET."

Establish a Baseline for the Chromatogram

28. The baseline will be established by analyzing a bag of ultrazero air (a BLANK sample). Connect the "zero" bag to the PROBE IN CONNECTION. Open the bag. To initiate the analysis, locate the ANALYSIS block and press the START/STOP key. The instrument will respond: "PROBE IN?" Press ENTER.
29. As soon as the ENTER key is pressed, the pump should start and run 10 seconds. If the pump does not start, inform the instructor.
30. Allow the chromatogram to be generated. Examine the baseline for significant drift or extraneous peaks. The baseline should be flat and smooth. Repeat this procedure until a stable (zero slope) baseline is obtained or until the instructor informs you to stop.

Analyze the Standard Gas Bag

31. For this exercise, we will use the chemicals in Library 1 as the standard. The "standard gas bag" will be used to check retention times and allow you to see a chromatogram.
32. Connect the "sample bag" bag to the PROBE IN CONNECTION. Open the bag. To initiate the analysis, locate the ANALYSIS block and press the START/STOP key. The instrument will respond: "PROBE IN?" Press ENTER.
33. Allow the chromatogram to be generated. This will take 600 seconds (the analysis time we selected).
34. At the end of the chromatogram, the printout will print the peak numbers that exceed the area setting, the identity of the peaks (if they match the retention times in the library) and the concentration of identified peaks. Consult the instructor for the expected results. If the peaks are not properly identified, a update adjustment or calibration run will be necessary. See *Updating the Library* and *Creating a Library* before analyzing any samples.

Updating the Library

35. If library does not recognize all of chemicals in the standard, the library should be updated.
36. Select a peak (one that you can identify) as a reference point. Press the CAL key. The instrument will request a plotter peak number. Enter the peak number you have selected. Press ENTER.
37. The instrument will request an ID number. Look at the previous printout of the library. Enter the number for the chemical that matches the peak. Press ENTER.
38. The instrument will request a concentration. Enter the concentration of the compound corresponding to the plotter peak used. Press ENTER.

39. The plotter will print out a listing of the peaks from the recent analysis and hopefully identify the peaks using retention times and peak areas adjusted by the reference peak.

Creating a Library

40. Connect the "sample bag" bag to the PROBE IN CONNECTION. Open the bag. To initiate the analysis, locate the ANALYSIS block and press the START/STOP key. The instrument will respond: "PROBE IN?" Press ENTER.
41. Allow the chromatogram to be generated.
42. The information from the chromatogram must be stored in the library **IMMEDIATELY FOLLOWING** completion of the analysis. **IF ANY OTHER KEY IS PRESSED BEFORE STEP #43, THE STANDARD CHROMATOGRAM WILL NEED TO BE GENERATED AGAIN TO UTILIZE ITS INFORMATION.**
43. Locate the LIBRARY block and press the STORE key. The instrument will prompt for:
- PLOTTER PEAK #: Select the number of the first peak of interest on the chromatogram and press ENTER.
 - CHEMICAL NAME: Select the name of the compound using the alpha-numeric keys on the key pad. After the name is complete press ENTER. (To change to numbers, press the CAL (NUM) key. This key must also be pressed again to return to letters.)
 - CONCENTRATION (in ppm): Select the actual concentration of the compound in ppm. Press ENTER.
 - LIMIT VALUE: The limit value is the concentration, which if exceeded, causes the plotter to print the concentration value in red instead of green. This "flags" the compound. Press ENTER. This will instruct the instrument to use 0 as the limit, so all concentrations will be in red.
 - This procedure is repeated for subsequent compounds in the chromatogram by pressing the STORE key and following steps a through d.
 - To check the contents of the library, press CAL. The instrument prompts with "PLOTTER PEAK #?" ENTER TO RELIST. Press ENTER. The plotter will print out the added compounds and their concentrations.

Note: DO NOT enter a value here or the instrument will prompt for recalibration.

Editing the Library

44. A compound can be added to the library after any analysis. A compound can be added to the library even if it is already in the library. However, the new entry will not replace the old entry. There will be two listings for the compound.
45. To remove a compound from the library, first press EDIT.
46. The instrument will prompt with "ID NUMBER." Enter the ID number for the compound in the library. The instrument will list the name of the compound.
47. Press CLEAR, then press ENTER. The instrument will respond with "COMPOUND REMOVED FROM LIBRARY."
48. Repeat for any additional compounds.

Analyze the Samples

49. Using steps 31 through 34, analyze the unknown samples provided.
50. **IMPORTANT! DO NOT USE ANY GAS BAGS**, other than those provided by the instructors, **WITHOUT THE PERMISSION OF THE INSTRUCTORS**. High concentrations can contaminate the column.

Exercise Shutdown

51. When sample analysis is complete, do not turn the instrument off.

Shutdown (Overnight)

52. Generate a chromatogram of the baseline to ensure that there are no residual materials in the column.
53. Locate the POWER block and press the OFF key. The instrument will respond with "ENTER=OFF." Press ENTER.
54. Adjust the flow rate for the DETECTOR OUT to 5 ml/min. Make sure the air supply is adequate for overnight operation.

Shutdown (Long Term)

55. Follow the same steps as in *Shutdown (Overnight)*.
56. Disconnect the power cord from the AC source.
57. Before shipping, drain the carrier gas supply reservoir.

EXERCISE #8

Sampling Pumps and Collection Media

OBJECTIVE

Participants will assemble a variety of sampling trains and calibrate them using an electronic bubble meter. They will also check the pump's flow compensator. The students will review sample results and evaluate exposure levels.

PROCEDURE

The class will be divided into teams. Each team will be given a Gilian® HFS 113UT air sampling pump.

The instructor will explain the operation of the Gilian® HFS 113UT sampling pump.

The students will calibrate the Gilian® sampling pump using different media and an electronic bubble meter.

Demonstration: Calibration of Gilian® pump with filter media using a bubble-meter (page 82).

Station 1: Calibration of Gilian® pump with filter media and with sorbent tube media using an electronic bubble-meter (page 85).

Station 2: Check flow compensator of Gilian® pump using Gilian® Calibrator Pack (page 92).

Note: The procedures shown here apply only to this specific sampling pump. The actual procedures for other pumps may vary. Consult the manufacturer's instructions for the pump you use in the field.

After calibrating their sampling pump, the students will look at sampling results and calculate concentration levels (page 94).

OPERATION AND CONTROLS OF GILIAN® HFS 113UT SAMPLER

The Gilian® HFS 113UT sampler is a lightweight, battery-powered air sampling pump. It has a high flow range—0.5–3.5 liters per minute (lpm) and a low flow range—1–500 cubic centimeters per minute (cc/min). It has a built-in timer to shut off the pump after a preset time. The pump is equipped with a flow compensation control that provides for constant air flow from the pump at any preset flow within its performance limits.

The following is a brief description of the controls for operating the pump.

1. **ON - OFF Switch.** This turns pump on and off.
2. **PRESS TO TEST Button.** When the pump is on, pressing this button gives battery power indication and also gives an elapsed time indication in TIME MIN window. If the pump has stopped because of end of time or fault, pressing this button before turning the pump off gives the pump run time.
3. **PROGRAMMABLE TIMER.** Allows operator to set sample time from 10 minutes to 990 minutes in ten minute increments. Note: The pump will not start if the timer is set at 00. When setting the timer, the dials should be turned clockwise past the zero point several times.
4. **BAT CK - Battery Check.** Turn on pump and press the test button. If the BAT CK illuminates, then the battery is fully charged.
5. **FAULT.** This light illuminates and the pump shuts down, if the pump is unable to maintain the preset flow rate.
6. **TIME OUT.** This illuminates when the pump stops at the programmed time.
7. **FLOW ADJUST.** Turning clockwise increases flowing; turning counterclockwise decreases flow.
8. **PUMP INLET.** Inlet to pump. Point where tubing and sampling media are connected.
9. **DISCHARGE AIR CAP SCREW.** Removing this screw provides access to discharge port. Inserting adapter allows pump to be used to fill gas bag.
10. **REGULATOR SHUTOFF CAP SCREW.** Removing screw provides access to the regulator shutoff valve. The valve is used to switch the pump from high to low flow.
11. **FLOW METER.** Rotameter used to show flow. Read center of flow meter ball. Reading is $\pm 20\%$ of true flow.

DEMONSTRATION: CALIBRATING GILIAN® PUMP USING A BUBBLE METER

During this demonstration, the Gilian® pump will be calibrated for lead particulate sampling. The NIOSH analytical method for lead sampling (Method 7802) uses a 0.8- μ cellulose ester membrane filter. The appropriate filter is provided with the calibration setup. The recommended flow rate is between 1 and 4 liters per minute. For this exercise, calibrate the pump to about 2 liters per minute (between 1.8 and 2.2 is okay). The important thing is to know the actual flow rate of your pump. Step 4 explains how to convert the pump to the high flow range.

BUBBLE METER PREPARATION

During this step, the Gilian® pump will be calibrated using an inverted buret and soap bubbles (bubble meter). This method is considered a primary calibration method because the buret volume and the stopwatch time can be traced to an original standard.

1. Check the calibration set-up (Figure 1). It should contain all the parts shown in the figure. If not, inform the instructor.
2. Wet the buret by pouring a small amount of soap solution into it, and tilting it up and down while rotating. Seal the outlet end to prevent soap from getting into the tubing.
3. Reassemble the calibration setup.

PUMP PREPARATION

4. Remove the Pump Regulator Shutoff Protective Cap. Turn the exposed screw clockwise until closed - **DO NOT OVERTIGHTEN**. Replace the protective cap.
5. Using the small screwdriver provided, set the programmable timer to 240 minutes. Turn each dial clockwise past zero several times before setting the time.
6. Turn the pump on.
7. Press the test button. The BAT CK light should illuminate or flicker.

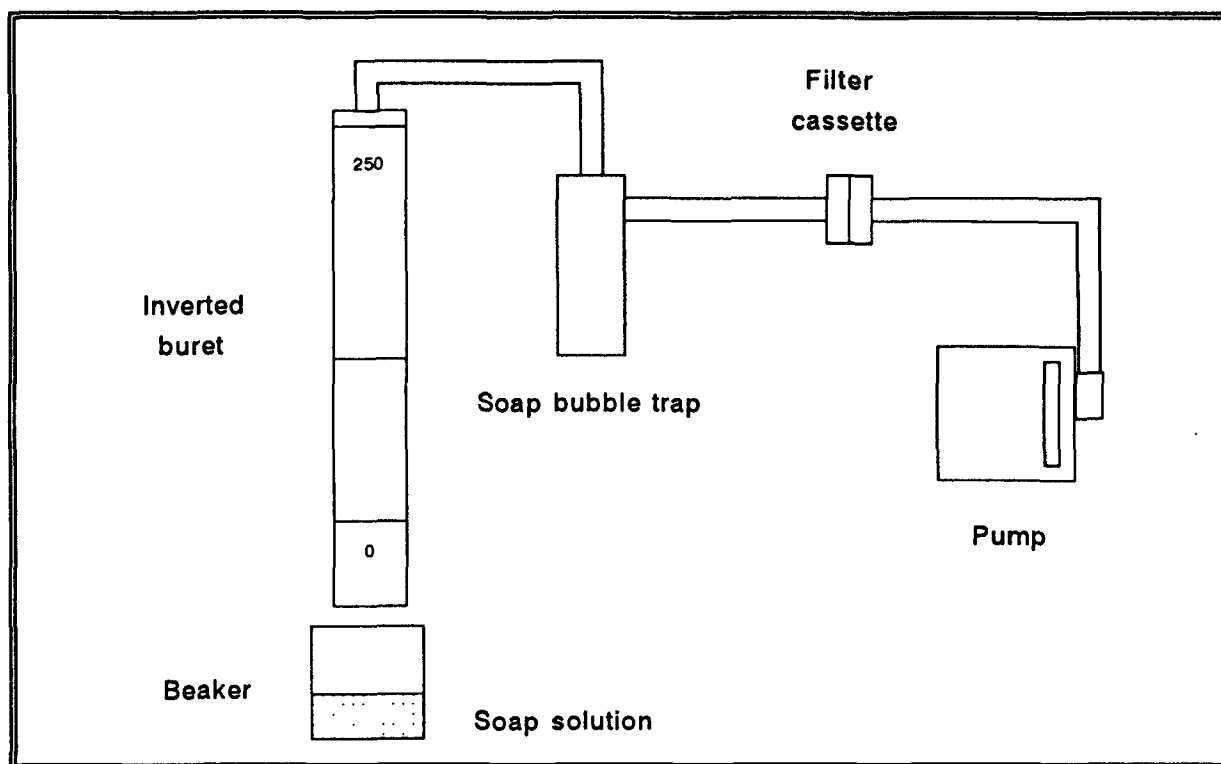


FIGURE 1. BUBBLE METER CALIBRATION SETUP

8. Connect the tubing and filter to the pump. The filter pad should be nearest to the pump. Connect the filter to the tubing attached to the bubble meter.
9. Start a bubble in the buret by briefly touching the surface of the soap solution to the open end of the buret. When the bubble passes the "0" mark, start the stopwatch. Stop the stopwatch when the bubble passes the "250" mark.
10. Flow rate is calculated using the following formula:

$$FLOW\ RATE\ (L/min) = \frac{VOLUME\ TRAVELED\ (ml)}{TIME\ (sec)\ BUBBLE\ TRAVELED} \times \frac{60\ sec/min}{1000\ ml/L}$$

11. Use *Data Sheet 1* to record your calibration data.

DATA SHEET 1

1. PUMP MFG. AND MODEL: _____
2. PUMP IDENTIFICATION #: _____
3. BATTERY CHECK _____ YES _____ NO
4. LOCATION/TEMP & BAROMETRIC PRESSURE: _____

5. CALIBRATION METHOD: _____
6. FLOW RATE CALCULATIONS

$$FLOW\ RATE\ (L/min) = \frac{VOLUME\ TRAVELED\ (ml)}{TIME\ (seconds)} \times \frac{60\ seconds/minute}{1000\ ml/L}$$

VOLUME TRAVELED	TIME	FLOW RATE	AVERAGE
_____	_____	_____	
	_____	_____	
	_____	_____	_____
	_____	_____	_____
	_____	_____	_____

(Continue calibration until three consecutive flow rates are within $\pm 5\%$ of the average.)

7. FLOW RATE: _____
8. ROTAMETER SETTING: _____
9. SIGNATURE: _____
10. DATE/TIME: _____

STATION 1: CALIBRATING THE GILIAN® PUMP USING AN ELECTRONIC BUBBLE METER

The Gilibrator™ is an example of an electronic bubble meter. It is a primary calibration method. A fixed volume is located in the center tube of the flow cell. A quartz-controlled timer is used to measure the travel time for a bubble between two sensors. A microprocessor calculates the volume per unit time. The flow rate is displayed in cc/min for this model.

The control unit will display the actual flow for each sample and will accumulate and average each successive reading.

AVERAGE - To display average and number of samples, depress and hold the AVERAGE BUTTON. Releasing the button will display the last flow reading. Pressing the button again and the number of reading made will be displayed. Release and the display returns to the last flow reading.

DELETE - To delete obvious false readings, push the DELETE BUTTON. This will delete the false information from the average and reset the average and sample number back to the previous reading.

RESET - To reinitiate the sequence, hit the RESET BUTTON. This will zero out all sample and average registers within the Control Unit. The Reset Button is also used if a malformed bubble is generated and has not been subtracted from the average by use of the DELETE Function.

GILIBRATOR™ PREPARATION

1. Remove the storage tubing between the air inlet and air outlet of the Gilibrator™. Pour a small amount of soap through the BOTTOM AIR INLET of the Gilibrator™ to thoroughly cover the bottom of the flow cell. Skip this step if already done.
2. Connect a pump to the UPPER AIR OUTLET using the piece of tubing provided.
3. Turn the regulator shutoff valve on the Gilian® pump (the screw under the brass cap on top of the pump) fully clockwise. **DO NOT OVERTIGHTEN**. Turn on the pump. Initiate soap film up the flow tube by rapidly pressing the CALIBRATOR BUTTON down and releasing. Repeat this procedure until a bubble travels the length of the tube without breaking.
4. After the Flow Tube walls have been "primed" (Step 3), turn on the Power switch of the Control Unit. Wait approximately 10 seconds while the system runs through its check sequence. The RUN LED will light at this time as well and a LO Battery indication and a series of five dashes will be displayed on the LCD Readout. Do not operate the Gilibrator until the RUN LED signal extinguishes. Ready operation is indicated by a series of 4 dashes.
5. Calibrate the pump using the following steps.

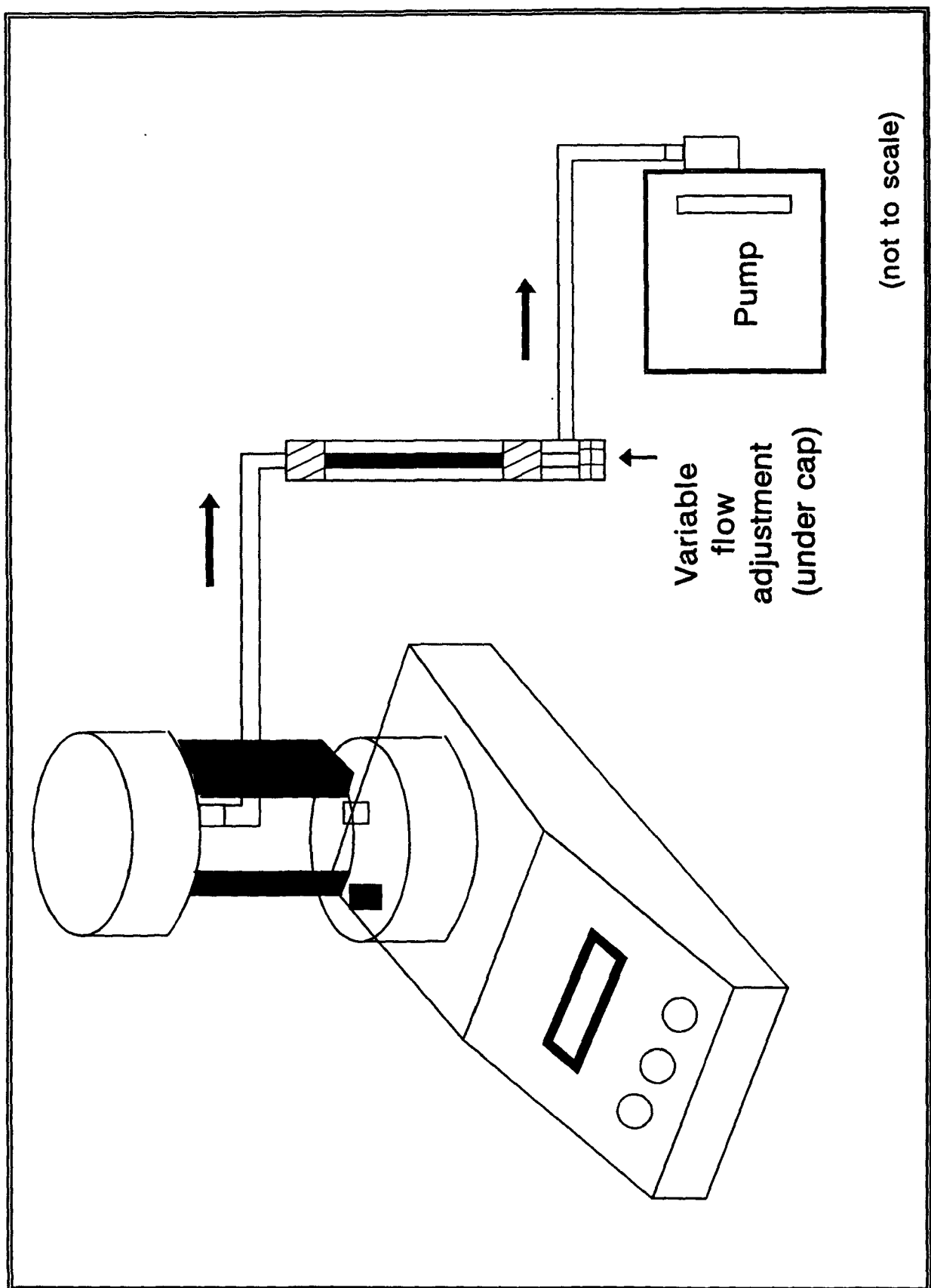


FIGURE 2. SAMPLE PUMP AND GILBRATOR™ SETUP

HIGH-FLOW CALIBRATION (1 to 4 liters/min)

6. Insert a filter cassette and tubing between the pump and the tubing attached to the calibrator.
7. Turn on the pump.
8. Depress the BUBBLE INITIATE BUTTON and hold to initiate 1 bubble up the Flow Tube. Release the button to initiate a second bubble up the flow tube. At low flow rates, the button can be depressed and released quickly for a single bubble.
9. After a bubble completes passage up the FLOW TUBE, a flow reading will appear on the LCD display.
10. Adjust the flow rate (pump adjustment) and repeat Steps 8 and 9 until you have a flow rate of about 2 liter/min.
11. RESET the calibrator.
12. Repeat Steps 8 and 9 until you have three consecutive readings that are within 5% of their average.
13. If the first set of 3 readings are not within the 5% allowable range, press the RESET Button. Then repeat step 15 for 3 more readings. The Reset Button is used because the Gilibrator™ averages all readings and not just the last 3. If the first reading was outside the 5% limits, you wouldn't know till readings 2 and 3 were made. Readings 2, 3, and 4 may be within the limits, but you would not be able to check because reading 1 would still be in the average.
14. If a bubble breaks before completing the timing sequence, timing will continue until another bubble is generated to trip the second sensor. This will cause an erroneous reading and should be subtracted from the average by hitting the Delete Button.
15. Record each run, the average, and other pertinent information on *Data Sheet 2*

LOW-FLOW CALIBRATION (20–500 cc/min)

16. Connect the pump to the Gilibrator™ with a piece of tubing.
17. Turn on the pump.
18. Using the steps above, adjust the pump to about 1 liter/min.
19. Open the regulator shutoff valve (located under the brass cap on top of the pump) by turning it counterclockwise **at least 5 turns**.

20. Put a carbon tube in the sorbent tube holder. Connect the inlet side of the holder to the upper outlet of the calibrator (**Figure 2**). Connect the outlet side of the holder to the pump inlet.
21. Depress the Bubble Initiate Button to initiate a bubble up the Flow Tube. After the bubble completes passage up the Flow Tube, a flow reading will appear on the LCD display.
22. Remove the knurled cap from the end of the tube holder. Repeat Step 21 and adjust the variable flow controller screw to get the desired flow rate. For this exercise, try to obtain about 50 cc/min.
23. RESET the calibrator after each run if not at the desired flowrate. Reset after each flow adjustment. Do three runs at the desired flow rate. Record your results on *Data Sheet 3*.

SHUTDOWN

24. Turn off the pump.
25. Turn off the calibrator.
26. Remove the air sampler from the Gilibrator™. Replace the Storage Tubing between the upper and lower cell chambers.
27. Disconnect the pump from the tube holder.
28. Replace the cap on the tube holder.

DATA SHEET 2

1. PUMP MFG. AND MODEL: _____
PUMP IDENTIFICATION #: _____
BATTERY CHECK ____ PASS ____ FAIL
2. CALIBRATOR MFG. AND MODEL: _____
CALIBRATOR IDENTIFICATION #: _____
3. COLLECTION MEDIA: _____
4. LOCATION/TEMP & BAROMETRIC PRESSURE: _____

5. FLOW RATES: (Continue calibration until three consecutive flow rates are within $\pm 5\%$ of average.)

FLOW RATE	AVERAGE	FLOW RATE	AVERAGE
_____		_____	_____
_____		_____	
_____	_____	_____	
_____		_____	_____

6. ROTAMETER SETTING: _____
7. FLOW RATE: _____
8. SIGNATURE: _____
9. DATE/TIME: _____

DATA SHEET 3

1. PUMP MFG. AND MODEL: _____
PUMP IDENTIFICATION #: _____
BATTERY CHECK _____ PASS _____ FAIL
2. CALIBRATOR MFG. AND MODEL: _____
CALIBRATOR IDENTIFICATION #: _____
3. COLLECTION MEDIA: _____
4. LOCATION/TEMP & BAROMETRIC PRESSURE: _____

5. FLOW RATES: (Continue calibration until three consecutive flow rates are within $\pm 5\%$ of average.)

FLOW RATE	AVERAGE	FLOW RATE	AVERAGE
_____		_____	_____
_____		_____	
_____	_____	_____	
_____		_____	_____

6. FLOW RATE: _____
7. SIGNATURE: _____
8. DATE/TIME: _____

STATION 2: CHECKING GILIAN® PUMP WITH CALIBRATOR PACK

The Gilian® Calibrator Pack has precision rotameters that can be used to calibrate a pump. A rotameter is considered a secondary calibration standard since it needs to be calibrated or checked with a primary calibration method periodically. The pack also has a magnehelic to produce a pressure drop along the flow of a pump. This, in combination with the rotameters, can be used to check the constant flow compensator on the Gilian® pump.

In this step, the precision rotameter will be used to check the constant flow compensator.

COMPENSATOR CHECK

1. Remove the Regulator Shutoff Protective Cap on the pump. Turn the exposed screw clockwise until closed - **DO NOT OVERTIGHTEN**. Replace the protective cap.
2. On the Calibrator pack, move the BYPASS/CAL switch to the BYPASS position.
3. Move the CAL SELECT (V2) switch to the upward position (3 liters/minute).
4. Connect the pump to the PUMP SUCTION (B1) outlet on the calibrator pack.
5. Turn on the pump.
6. Adjust (on the pump) the flow rate so that precision rotameter on the calibrator (not the pump rotameter) reads "3.0" (3 liters/min or 3000 cc/min). The flow rate is read at the center of the rotameter ball.
7. Move the CAL/BYPASS switch to the CAL position.
8. Turn the V3 knob until the magnehelic dial reads 10 inches of back pressure.
9. Read the flow rate on the rotameter. If the difference in flow rates with and without back pressure is more than $\pm 5\%$ (i.e., if the flow rate is not between 2850 and 3150), the pump needs adjustment. Consult the instructor.
10. Move the BYPASS/CAL switch to the BYPASS position.
11. Move the CAL SELECT (V2) switch to the downward position (1 liter/minute).
12. Adjust the flow rate to "1.0" (1 liter/min or 1000 cc/min) - reading the precision rotameter on the calibrator.
13. Move the BYPASS/CAL switch to the CAL position.
14. Turn the V4 knob until the magnehelic dial reads 20 inches of back pressure.

15. Read the flow rate on the rotameter. If the difference in flow rates with and without the back pressure is more than $\pm 5\%$ (i.e., if the flow rate is not between 950 and 1050), the pump needs adjustment. Consult the instructor.

SHUTDOWN

16. When completed with the compensator check, turn off the pump and disconnect the pump from the pack.

QUESTIONS AND CALCULATIONS

1. Calculate the concentrations in the sampled atmospheres based on the following information.

Units: 1000 liter = 1 m³
 1000 ml = 1000 cc = 1 liter
 1 mg = 1000 micrograms

- (A) Lead samples. Pump flow rate = 2.0 liters per minute.

SAMPLE DURATION	LAB ANALYSIS	AVERAGE CONCENTRATION
4 HR	0.041 mg	
2 HR	0.029 mg	
2 HR	0.008 mg	

To calculate the Average Concentration (for each sample):

$$C = \frac{\text{mg chemical}}{\text{sample volume (m}^3\text{)}}$$

where:

$$\text{sample volume (m}^3\text{)} = \text{pump flow rate (liters/minute)} \times \text{sample time (minutes)} \times \frac{1 \text{ m}^3}{1000 \text{ liters}}$$

To calculate an 8-hour TWA:

$$8 \text{ hour TWA} = \frac{C_1 T_1 + C_2 T_2 + \dots C_n T_n}{8 \text{ hours}}$$

where T is sample time in hours. Minutes can be used for T if 480 minutes is used instead of 8 hours in equation.

(B) Solvent vapor sampling. Flow rate = 50.0 cc/min.

SAMPLE TIME	CONCENTRATION (ppm)		
	TOLUENE	XYLENE	ACETONE
1 HR	10	5	ND
2 HR	32	11	ND
1 HR	21	8	100
15 MIN	175	70	300
15 MIN	140	50	1000
15 MIN	100	67	820
30 MIN	93	40	1000
15 MIN	85	30	50
30 MIN	54	10	45
2 HR	10	ND	30

- Calculate an 8-hour TWA exposure for the three chemicals.
- Calculate an 8-hour TWA exposure for the mixture. Is this calculation valid?

(C) Do any of the concentrations in (A) and (B) exceed an exposure limit?

2. Calibration of a pump prior to sampling gave a flow rate of 2.0 liters/minute. Calibration after sampling gives a flow rate of 1.8 liters/minute. What do you do?

EXERCISE #9

Field Exercise

OBJECTIVE

Using the instruments and information provided, participants will:

1. Perform a survey of the zones on the "hazardous waste site."
2. Characterize the "hazards" present at each "zone" on the site.
3. Identify as completely as possible the materials present on the site.
4. Quantify the airborne concentrations in each "zone" and evaluate the risk associated with these concentrations.

PROCEDURE

The class will be divided into teams. Each team will select a leader/spokesperson. Each team will receive the same equipment. The equipment available is the same equipment used earlier in the week. Before each entry, the team must submit plan of action for that entry to an instructor.

The "site" simulates a much larger site. It is divided into six zones. A description of each zone is on the next page. A "map" of the site also follows. Treat the readings obtained with the instruments taken inside the containers as representing the average airborne concentrations in the "zone."

DESCRIPTION OF EXERCISE AREA

ZONE 1:

100 to 200 drums. Some with "FLAMMABLE" labels.

ZONE 2:

About 100 drums. Some with "CORROSIVE" labels.

ZONE 3:

Box trailer containing drums. Records indicate that the following chemicals were in the load. (*Note:* This zone can be treated as a transportation incident separate from the site.)

- Acetone
- Methyl ethyl ketone
- Methyl isobutyl ketone
- Ethyl alcohol
- Butyl alcohol
- Toluene
- Benzene
- Xylenes
- 1,1,1-Trichloroethane
- Trichloroethylene
- Tetrachloroethylene

Readings taken in the drum represent readings at the trailer.

ZONE 4:

About 50 drums with "Waste Cleaner" labels.

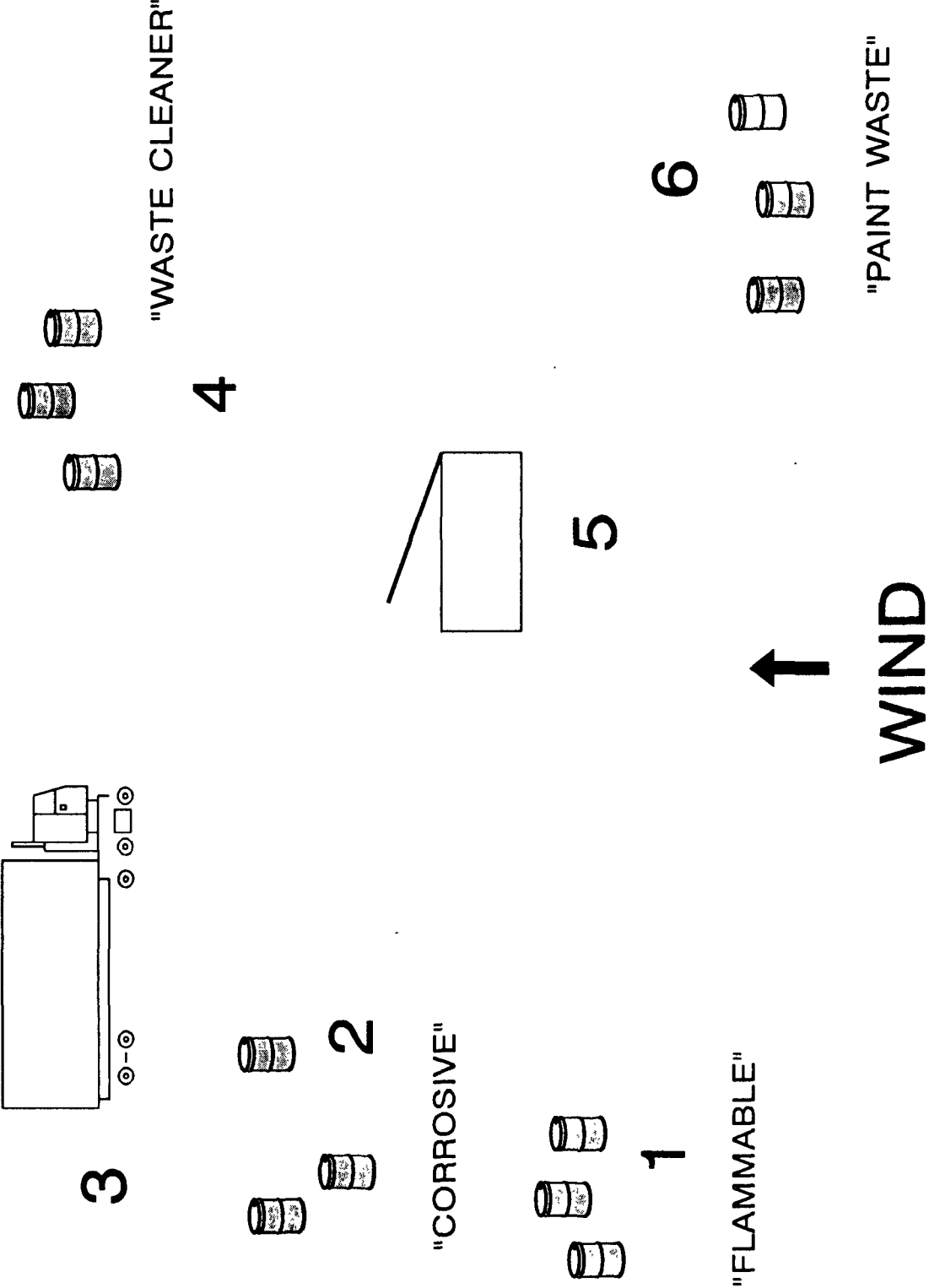
ZONE 5:

Opening to underground vault. The vault could contain many drums. Readings inside container are equivalent to readings taken inside vault (using extended probes).

ZONE 6:

50 to 100 drums. Some with hand-painted labels reading "Paint Waste."

"SITE" MAP



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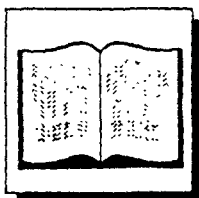


Personal Air Sampling and Air Monitoring Requirements Under 29 CFR 1910.120

Office of Emergency and Remedial Response
Emergency Response Division MS-101

Quick Reference Fact Sheet

Background and Purpose



Under the authority of Section 126 of the Superfund Amendments and Reauthorization Act of 1986 (SARA Title I), the U.S. Environmental Protection Agency (EPA) and the U.S. Occupational Safety and Health Administration (OSHA) issued identical health and safety standards to protect workers engaged in hazardous waste operations and emergency response. The OSHA regulations, codified at 29 CFR 1910.120, became effective on March 6, 1990 (54 FR 9294). On April 13, 1990, corrections to these regulations were published (55 FR 14072) to clarify certain medical surveillance requirements and to identify which employers must comply with 29 CFR 1910.120(p). The EPA regulations, published on June 23, 1989, at 54 FR 26654, incorporate the OSHA standards by reference and are codified at 40 CFR Part 311.

Although the two sets of standards contain identical substantive provisions, the EPA and OSHA standards address different audiences. In states that do not have an OSHA-approved program, federal OSHA standards protect all private and federal employees engaged in hazardous waste operations and emergency response; EPA worker protection standards protect all state and local government employees. In states that do have an OSHA-approved program, the state program covers all private, state, and local government employees; OSHA covers federal employees. The OSWER Fact Sheet, *Hazardous Waste Operations and Emergency Response (HAZWOPER): Uncontrolled Hazardous Waste Sites and RCRA Corrective Action* (OSWER Publication 9285.2-08FS, 1991), provides a general overview of the worker protection standards as they apply to operations conducted at uncontrolled hazardous waste sites.

OSHA requirements for monitoring at uncontrolled hazardous waste sites are codified at 29 CFR 1910.120(h). While the provisions outlined in this

section may be interpreted to include the collection of samples (i.e., surface wipes in the support area on lead-contaminated site), the purpose of this Fact Sheet is to summarize the HAZWOPER air monitoring and sampling aspects of these requirements. The Fact Sheet is composed of five parts: (1) Introduction to Air Monitoring and Air Sampling; (2) Air Monitoring Requirements Upon Initial Entry; (3) Air Monitoring Requirements After Initial Entry; (4) Conducting Air Monitoring and Sampling; and (5) Information Sources and Contacts.

Introduction to Air Monitoring and Air Sampling



The presence of hazardous materials at a site, as well as actions taken to address these materials, can result in the release of hazardous substances into the air. Chemical fires, transportation accidents, open or leaking containers, wind-blown dust, and site cleanup activities all produce emissions that can rapidly affect the health and safety of response personnel (site workers or emergency response) and the public. Hazardous atmospheres may be:

- Explosive (characterized by the presence of ignitable or explosive vapors, gases, aerosols, and dusts);
- Toxic/hazardous (characterized by the presence of vapors, gases, particulates, and aerosols);
- Oxygen-deficient (characterized by the consumption or displacement of oxygen in ambient air); or
- Radioactive (characterized by the presence of radioactive materials).



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The presence of one or more of these hazards is an important factor in determining subsequent actions that should be taken to protect workers, the community, and the environment. Their presence may dictate operations that are necessary to mitigate the likelihood of an incident, and will dictate safety considerations for response personnel.

OSHA requirements for air monitoring are set forth in the HAZWOPER standards at 29 CFR 1910.120(h). Specifically, §1910.120(h)(1)(i) states that monitoring must be performed "where there may be a question of employee exposure to hazardous concentrations of hazardous substances in order to assure proper selection of engineering controls, work practices and personal protective equipment [PPE] so that employees are not exposed to levels which exceed permissible exposure limits [PELs], or other published exposure levels...." The regulations also require air monitoring for use in identifying health hazards in order to determine appropriate level of PPE. Once the appropriate PPE is selected, personal air sampling should be continued in order to ensure that personnel exposures are not exceeding these limitations.

NOTE: OSHA does not define the term "air monitoring." Rather, OSHA uses this term to refer to both monitoring using direct reading instrumentation and to air sampling using personal sampling pumps or other quantitative methods. However, in this Fact Sheet, the term "air monitoring" refers to the use of direct reading instruments producing instantaneous data, while the term "air sampling" refers to the use of a sampling pump and collection media that produce samples that must be sent to a laboratory for analysis. The specific distinctive features of each are:

Air monitoring:

- Provides "real-time" results;
- Provides rapid response;
- Is generally not compound-specific;
- Has limited detection levels; and
- May not detect certain classes of compounds.

Air sampling:

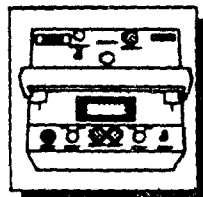
- Can be compound- or class-specific;
- Provides greater accuracy of detection;
- Requires more time for results; and
- Requires additional pumps, media, analytical support.

One example of the difference between air monitoring and air sampling is that air monitoring can be performed to identify the existence of a hazardous atmosphere during initial site entry, while air sampling is performed to identify and quantify an employee's personal exposure to a hazardous chemical or range of hazardous chemicals. Further, air monitoring data are instantaneous and are useful in comparing conservative action guidelines to determine an appropriate level of protection relative to the work activity. Air sampling data are information used to compare an employee's exposure to OSHA 1971 time-weighted average PELs (PEL-TWA), PEL-ceiling (PEL-C), the American Conference of Governmental Industrial Hygienists time-weighted average Threshold Limit Values (TLV-TWA), and associated values (STEL,C).

In addition to the requirements at 29 CFR 1910.120(h), OSHA mandates air sampling for specific chemical contaminants under 29 CFR 1910.1000, which lists approximately 428 substances in Tables Z-1-A, Z-2, and Z-3. OSHA also has comprehensive health standards that have additional PELs and other requirements (see **Highlight 1**). Consult individual standards for specifics.

NOTE: The U.S. Court of Appeals, Eleventh Circuit, issued a decision on July 7, 1992, vacating the "Final Rule" of the Air Contaminants Standard. A decision was made on March 22, 1993, not to appeal to the Supreme Court, and the Eleventh Circuit Court's decision stands. Employers and Employees can find the 1971 permissible exposure limits that are now in effect listed in the Air Contaminants Standard, in the columns headed "Transitional Limits" in Table Z-1-A and in Tables Z-2 and Z-3 in 29 CFR 1910.1000 (1989 or later).

Air Monitoring Requirements Upon Initial Entry



During the initial site entry, information is gathered to evaluate site-specific risks and hazards. This information is used to select and develop site-specific engineering/administrative controls, PPE, medical monitoring, and air sampling requirements. **Highlight 2** identifies some of the contaminant and hazard risks that may be encountered during initial site entry.

Highlight 1 SUBPART Z, TOXIC AND HAZARDOUS SUBSTANCES

29 CFR 1910.1001	Asbestos, tremolite, anthophyllite, and actinolite
29 CFR 1910.1002	Coal tar pitch volatiles (interpretation of term)
29 CFR 1910.1003	4-Nitrobiphenyl
29 CFR 1910.1004	alpha-Naphthylamine
29 CFR 1910.1006	Methyl chloromethyl ether
29 CFR 1910.1007	3,3'-Dichlorobenzidine (and its salts)
29 CFR 1910.1008	bis-Chloromethyl ether
29 CFR 1910.1009	beta-Naphthylamine
29 CFR 1910.1010	Benzidine
29 CFR 1910.1011	4-Aminodiphenyl
29 CFR 1910.1012	Ethyleneimine
29 CFR 1910.1013	beta-Propiolactone
29 CFR 1910.1014	2-Acetylaminofluorene
29 CFR 1910.1015	4-Dimethylaminoazobenzene
29 CFR 1910.1016	N-Nitrosodimethylamine
29 CFR 1910.1017	Vinyl chloride
29 CFR 1910.1018	Inorganic arsenic
29 CFR 1910.1025	Lead
29 CFR 1910.1027	Cadmium
29 CFR 1910.1028	Benzene
29 CFR 1910.1029	Coke oven emissions
29 CFR 1910.1043	Cotton dust
29 CFR 1910.1044	1,2-dibromo-3-chloropropane
29 CFR 1910.1045	Acrylonitrile
29 CFR 1910.1047	Ethylene oxide
29 CFR 1910.1048	Formaldehyde
29 CFR 1910.1101	Asbestos (Applies in lieu of revised standards governing occupational exposure to asbestos, tremolite, anthophyllite, and actinolite)

Air monitoring techniques are used to assess the risks that may be present during initial site entry. As specified at 29 CFR 1910.120(h)(2), air monitoring must be conducted during the initial site entry to identify:

- IDLH conditions;
- Exposure over permissible exposure limits or published exposure levels;
- Exposure over radioactive materials dose limits; or
- Exposure to other dangerous conditions (e.g., presence of flammable atmospheres or oxygen-deficient environments).

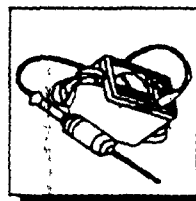
Highlight 2 CONTAMINANT AND HAZARD RISKS DURING INITIAL SITE ENTRY

- Exposure exceeding the OSHA PELs or other published exposure levels;
- Exposure to immediately dangerous to life and health (IDLH) concentrations;
- Exposure through skin absorption and irritation (chemical or biological);
- Eye irritation;
- Explosions resulting from shock-sensitive substances and flammable atmospheres;
- Confined space-entry;
- Injury from physical hazards, and
- Exposure to radioactive (ionizing radiation) materials.

NOTE: While required in 29 CFR 1910.120 (h)(2), monitoring for radioactive materials under initial entry conditions is not an "air" monitoring technique. If the main concern is to identify exposure over radioactive material dose limits, the contaminant of interest is gamma radiation. Gamma radiation is not air-matrix dependent.

Air sampling is not usually performed during the initial entry. Instead, information about the potential chemical hazards is gathered during the initial entry and used to make decisions about air sampling needs. For any contaminants discovered during the initial entry that are regulated by 29 CFR 1910.1000 or Subpart Z (see Highlight 1) or that could be considered hazardous, the air sampling needs must be assessed according to the requirements.

Air Monitoring Requirements After Initial Entry - Periodic Monitoring



Site conditions and atmospheric chemical conditions may change following the initial site characterization. As stated at 29 CFR 1910.120(h)(3), periodic monitoring must be conducted when "the possibility of an IDLH condition or flammable atmosphere has developed or when there is indication that exposures may have risen over permissible exposure limits or published exposure

levels since prior monitoring." **Highlight 3** identifies situations that call for periodic monitoring required at 29 CFR 1910.120(h)(3)(i-iv).

**Highlight 3
SITUATIONS THAT REQUIRE
PERIODIC MONITORING**

- When work begins on a different portion of the site;
- When contaminants other than those previously identified are being handled,
- When a different type of operation is initiated (e.g., drum opening as opposed to exploratory well drilling); or
- When employees are handling leaking drums or containers, or working in areas with obvious liquid contamination (e.g., a spill or a lagoon).

Once cleanup activities begin on-site, 29 CFR 1910.120(h)(4) requires employers to "monitor those employees likely to have the highest exposures to hazardous substances and health hazards likely to be present above permissible exposure limits or published exposure levels by using personal sampling frequently enough to characterize employee exposures." Air sampling for high-risk employees is performed to identify the "worst-case exposure." If the worst-case exposure is above the PEL, then monitoring should be conducted to identify all employees likely to be above those limits. (Note: It is not required to monitor employees engaged in site characterization operations covered under 29 CFR 1910.120(c). Appropriate PPE based upon the preliminary evaluation is required.)

Post-initial entry situations that require periodic monitoring also should be characterized by air sampling, as appropriate, and should be determined by a competent health and safety professional. Air sampling information can be compared to the air monitoring data for the same period of time to: (1) illustrate trends in the accuracy of the air monitoring data; (2) develop a correlation to the air monitoring readings; and (3) develop better air monitoring action guidelines. Air monitoring data may also be used to determine when further sampling is needed (i.e., if site conditions have changed).

Personal sampling generally is not used to characterize overall site air quality. However, air sampling conducted in areas of high concentration may assist in determining whether personal sampling is necessary. Air sampling may also assist On-Scene Coordinators (OSCs), Remedial Project Managers (RPMs), or other site managers in determining whether chemical contaminants covered under 29 CFR 1910.1000, Subpart Z, need to be monitored.

An air sampling strategy outlined in the site-specific health and safety plan must address frequency and type of air monitoring, personal monitoring, and environmental sampling (29 CFR 1910.120(b)(4)(ii)(E)). **Highlight 4** identifies additional information that should be provided in area and personnel air sampling strategies.

**Highlight 4
EXAMPLES OF ELEMENTS TO INCLUDE IN
AN AREA AIR SAMPLING STRATEGY**

- The locations where air sampling will be performed;
- The hazardous substances that will be sampled during the task;
- The duration of the sample;
- The equipment that will be used to sample for the different hazardous substances; and
- Collection of meteorological data.

**EXAMPLES OF ELEMENTS TO INCLUDE IN
A PERSONNEL AIR SAMPLING STRATEGY**

- Employee sampled;
- Tasks performed,
- Duration;
- Hazardous substances; and
- Equipment to be used.

Conducting Air Monitoring

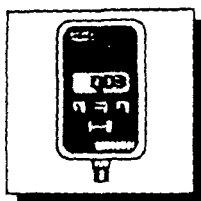


Table 1 at the end of this Fact Sheet, "Summary of Direct-Reading Air Monitoring Instruments," lists the direct-reading instruments (DRIs) used during air monitoring to characterize hazardous atmospheres. DRIs may be used to rapidly detect flammable or explosive atmospheres, oxygen deficiency, certain gases and vapors, and ionizing radiation. DRIs are the primary tools of initial site characterization. The information provided by DRIs can be used to: select appropriate protective measures such as personal protective equipment, evacuation, and other similar measures; determine the most appropriate equipment for further monitoring; and assist in developing optimum sampling and analytical protocols.

DRIs have limitations. For example, the Flame Ionization Detector (FID) and Photoionization Detector (PID) are commonly used at hazardous waste sites to monitor for a broad range of organics and some inorganics. However, they do not detect some particularly toxic agents such as hydrogen cyanide and hydrogen sulfide. Thus, these devices must be supplemented with other methods of detection (e.g., electrochemical sensors or colorimetric indicator tubes). Many DRIs designed to detect one particular substance may also detect other (cross sensitive) substances, thus rendering a "false positive." All DRI information should be interpreted with a certain degree of caution.

To characterize personal exposure, air monitoring should be performed in the breathing zone of the individual. Emission sources may be characterized through head-space monitoring (e.g. drums) or close-range monitoring, if this can be done safely. Emission source measurements are not representative of personal exposure.

Air monitoring instruments should be field-calibrated on a daily basis prior to the initial entry and/or any field activity. Calibration must be performed according to manufacturer's instructions. Field calibration should take place in field atmospheric conditions in a "clean" area, such as the command post. Calibration must be documented, either in a site logbook, or a logbook designated for instrument calibration records as required in the site safety plan (29 CFR 1910.120(b)(4)(ii)(E)).

Air monitoring data should be documented in the individual's field or the site logbook. Observations pertaining to the monitoring data (i.e., weather conditions, drum label information, activity performed

during monitoring, number/names of individuals being monitored, etc.) should be recorded with the monitoring data.

Conducting Air Sampling



Table 2 at the end of this Fact Sheet, "Common Air Sampling Methods and Media Used by the EPA/ERT," summarizes some sampling methods commonly used on hazardous waste sites. Personal air sampling is generally performed using a personal sampling pump capable of both low-flow (20-750 cc/min) and high-flow (1-4 L/min) operation. Low-flow operation with various media-packed tubes is used to sample volatile organic materials and acid gas mists. High-flow operation with various filter media or bubbler/impinger solutions is generally used to sample particles, particulate aerosols, and inorganic gases. Personal air sampling is performed for the duration of the workshift. Employees with the highest exposure potential wear the sampling pumps with the sample media positioned on their shoulders and the inlet of the filter or tube facing down toward the chest. (Applying protective "covers" often eases decontamination of the pumps.) Personal air sampling results are generally compared to the 8-hour PEL-TWA.

Sampling for comparison to the PEL-Short-Term Exposure (PEL-STEL) will require collecting a 15-minute sample at higher flow rates. PEL-STEL and PEL-C sampling may be run throughout the workshift alongside the PEL-TWA sampling. PEL-STEL and PEL-C sampling may be performed once every hour throughout the workshift, at the times of highest potential exposure. Judgment should be used when identifying times of highest potential exposure and performing a PEL-STEL and/or PEL-C sampling event simultaneously during this high-risk exposure period.

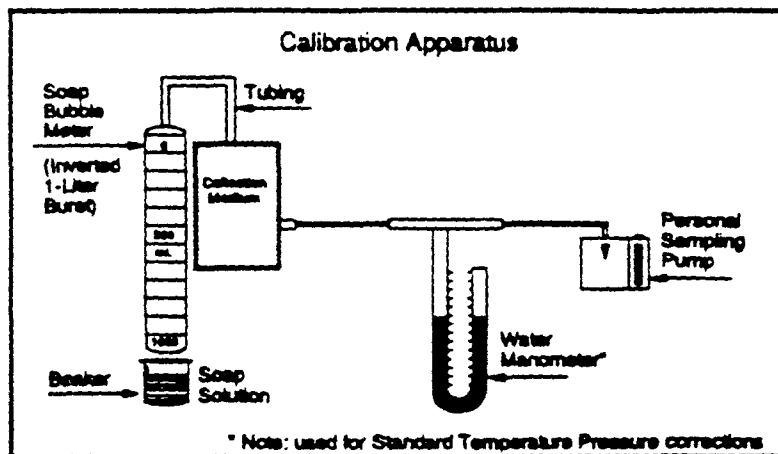
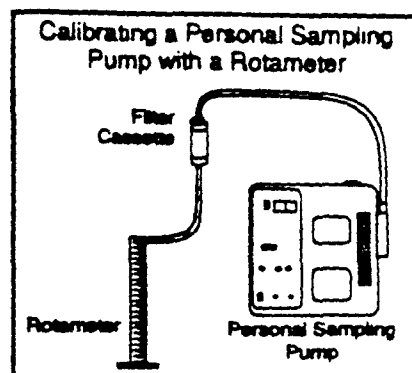
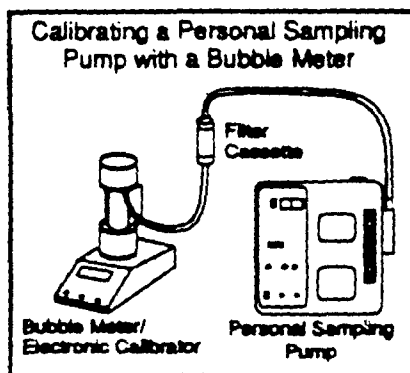
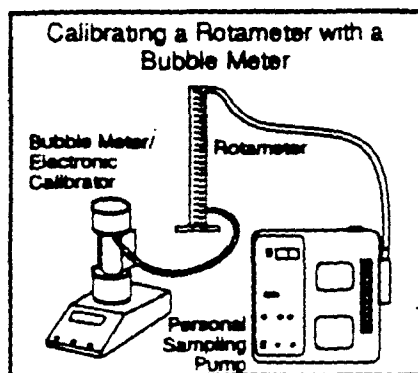
There are a number of references that list standard methods for performing personal air sampling. OSHA and the National Institute for Occupational Safety and Health (NIOSH) publish two sets of the most widely used personal air sampling methods. Both NIOSH and OSHA methods are "recipes" for performing both air sampling and chemical analysis. The methods outline the sampling device, collection media, and flow rate at which to set the sampling device. OSHA and NIOSH usually include in the methods any interferences that may bias the sampling. The EPA/Environmental Response Team (EPA/ERT) has developed standard sampling methods that incorporate existing NIOSH and OSHA methods. The "Information Sources" section of

this Fact Sheet identifies sources to obtain more information on these methods.

Before a sampling method is chosen, the laboratory should be contacted to determine whether it can perform the desired analysis. The EPA/ERT recommends using laboratories accredited by the American Industrial Hygiene Association (AIHA) for performing analysis on personal air samples. A list of AIHA-accredited laboratories may be obtained by contacting the AIHA (see the "Contacts" section of this Fact Sheet for AIHA's address and phone number).

As with DRIs, sampling pumps must be calibrated prior to use. The goal of calibrating the personal sampling pump is to set, and ensure that the pump can maintain, a known flow rate. Calibration requires a pump, a sampling train (including the sample media and all connecting tubing), and a primary standard-flow indicator, such as a bubble meter (Buck calibrator/Gillibrator), or an inverted buret with bubble mixture. A secondary standard flow indicator, such as a rotameter, may be used to calibrate the pump as long as the secondary standard has been previously calibrated to a primary standard. **Highlight 5** illustrates several different methods of calibration.

Highlight 5 EXAMPLES OF CALIBRATION METHODS



Source: Manual of Analytical Methods (Volume 1, 3rd Edition)
(NIOSH, 1984, Pub No. 84-100)

Highlight 6
EXAMPLES OF PERTINENT INFORMATION
FOR AIR SAMPLING DOCUMENTATION

- Name of employee sampled
- Task performed during sampling period
- Suspected hazardous substances.
- Level of PPE
- Type of collection media,
- Flow rate of the calibrated pump (pre- and post-sampling event),
- Duration of the sample;
- Date of sampling event,
- Location of sampling event,
- Environmental conditions during sampling event (e.g., temperature, Rh, wind speed, etc.);
- Unique sample number,
- Volume of air sampled during event;
- Any special handling requirements; and
- Analytical holding times

Documentation of all aspects of the sampling monitoring event is critical for both air monitoring and air sampling. Documentation provides information for data interpretation and, in the case of air sampling, tracking the sample from the sample taker to the laboratory. Air sampling documentation is more formalized than documentation for air monitoring. **Highlight 6** identifies pertinent information that must be documented for air sampling.

If sampling media (tubes or filters) are changed throughout the day to prevent overloading, sampling duration for that media must be noted. Judgment must be used in deciding how to document such a sampling event. Each tube/filter may be designated a unique number and treated as a single sample, or each tube/filter may be designated the sample number with different consecutive letter of the alphabet attached. The tubes or filters are unique, but together they represent one complete workshift sample. Setting up and performing personal air sampling generally requires more preparation time than air monitoring; however, in both cases, the correct instrument and sampling train must be chosen, the instrument and sampling train must be calibrated, and the monitoring or sampling event must be observed.

TABLE 1
SUMMARY OF DIRECT-READING AIR MONITORING INSTRUMENTS

Principle of Detection and Monitoring Need	Instrument	Features	Limitations
Wheatstone Bridge Filament <i>Monitoring Need: Combustible Gas</i>	Combustible Gas Indicator	<ul style="list-style-type: none"> ♦ Calibrated to pentane, hexane, or methane ♦ Nonspecific detector for combustible gases measures gas concentrations as a percentage of lower explosive limit (LEL) ♦ Lightweight, portable, and easy to use ♦ Visual and audible alarms (some models) ♦ Probe provides remote sensing capabilities ♦ 8- to 12-hour battery operating life for most models ♦ Accuracy varies depending upon the model, accuracies of ± 2 to 3 percent are attainable* 	<ul style="list-style-type: none"> ♦ Potential interferences or filament damage from leaded gasoline, silicones and silicates, which are more strongly adsorbed on catalyst than oxygen or gas in question. Membranes are available to minimize these effects ♦ Most models do not measure specific gases ♦ May not function properly in oxygen-deficient atmospheres (< 10 percent)
Chemical Cell <i>Monitoring Need: Oxygen Deficiency</i>	Oxygen Meter	<ul style="list-style-type: none"> ♦ Direct readout in percent oxygen ♦ Visual and audible alarms ♦ Lightweight, portable, and easy to use ♦ Probe provides remote sensing capabilities ♦ Accuracies of ± 1 percent are attainable, but depend on the particular model ♦ Generally 8- to 10-hour battery life 	<ul style="list-style-type: none"> ♦ High humidity may cause interference ♦ Strong oxidants may cause artificially high readout ♦ Oxygen calibrations are dependent on altitude and barometric pressure ♦ CO₂ "poisons" detector cell
Chemical Sensor Wheatstone Bridge Filament <i>Monitoring Need: Combustible Gas/Oxygen Deficiency</i>	Combination Oxygen Meter and Combustible Gas Indicator	<ul style="list-style-type: none"> ♦ Calibrated to pentane, hexane, or methane ♦ Measure percent oxygen and gas concentration as a percentage of LEL ♦ Both visual and audible alarms (some models) ♦ Remote sensing capabilities ♦ Lightweight, portable, and easy to use ♦ Accuracies of ± 2 percent are attainable* 	<ul style="list-style-type: none"> ♦ Same limitation as oxygen meters and combustible gas detectors ♦ In certain units, acid gases and high CO₂ concentrations shorten the life of oxygen sensor/cells ♦ Certain units require a conversion factor for true specific compound response readings ♦ In certain units, oxygen calibration is altitude dependent
Optical, Electrical, Piezoelectric <i>Monitoring Need: Aerosol/Particulate</i>	Aerosol/Particulate Monitor	<ul style="list-style-type: none"> ♦ Selectable ranges ♦ Particle size differentiation available ♦ Certain units have data logging capabilities 	<ul style="list-style-type: none"> ♦ Factory recalibration required on certain units ♦ Values represent total particulates: dust, mist, aerosols are all inclusive with no differentiation ♦ Cold weather may have adverse effect on detector ♦ High humidity and precipitation negatively affect meter response

* Manufacturer specifications. Actual field use may yield greater variations.

TABLE 1 (CONT'D)
SUMMARY OF DIRECT-READING AIR MONITORING INSTRUMENTS

Principle of Detection and Monitoring Need	Instrument	Features	Limitations
Photoionization Ultraviolet Light <i>Monitoring Need:</i> Toxic Gas/Vapors	Photo-ionization Detector (PID)**	<ul style="list-style-type: none"> ◆ Nonspecific gas and vapor detection for organics and some inorganics ◆ Not recommended for permanent gases ◆ Lightweight (4 to 9 lbs) and portable ◆ Sensitive to 0.1 ppm benzene. Sensitivity is related to ionization potential of compound ◆ Remote sensing capabilities ◆ Response time of 90 percent in less than 3 seconds ◆ More sensitive to aromatics and unsaturated compounds than the flame ionization detector (FID) ◆ 8-hour battery operating life; certain units with external interchangeable battery packs ◆ Audible alarm is available ◆ Certain units have data logging/computer interface capabilities ◆ Certain units available with calibration libraries ◆ Certain units available with interchangeable lamps 	<ul style="list-style-type: none"> ◆ Does not monitor for specific gases or vapors ◆ Cannot detect hydrogen cyanide or methane ◆ Cannot detect some chlorinated organics ◆ High humidity and precipitation negatively affect meter response ◆ Readings relative to calibration standard
Hydrogen Flame Ionization <i>Monitoring Need:</i> Toxic Gas/Vapors	Flame Ionization Detector (FID)	<ul style="list-style-type: none"> ◆ In the survey mode, it functions as a nonspecific total hydrocarbon analyzer; in the gas chromatograph mode, it provides tentative qualitative/quantitative identification (OVA-specific) ◆ Most sensitive to saturated hydrocarbons, alkanes, and unsaturated hydrocarbon alkenes ◆ Lightweight (12 lbs) and portable ◆ Remote sensing probe is available ◆ Response time is 90 percent in 2 seconds ◆ 8-hour battery operating life ◆ Sounds audible alarm when predetermined levels are exceeded 	<ul style="list-style-type: none"> ◆ Not suitable for inorganic gases (e.g., Cl₂, HCN, NH₃) ◆ Less sensitive to aromatics and unsaturated compounds than PID ◆ Requires skilled technicians to operate the equipment in the GC mode and to analyze the results (OVA-specific) ◆ Requires changes of columns and gas supply when operated in the GC (gas chromatography) mode in certain units (OVA-specific) ◆ Because specific chemical standards and calibration columns are needed, the operator must have some idea of the identification of the gas/vapor (OVA-specific) ◆ Substances that contain substituted functional groups (e.g., hydroxide (OH-) or (Cl-) chloride groups) reduce the detector's sensitivity

**UV sources vary in strength among available units (10.2ev, 10.6ev, 11.7ev). Each source has a range of compounds it cannot detect based upon ionization potentials. See manufacturer's literature for specifics.

TABLE 1 (CONT'D)
SUMMARY OF DIRECT-READING AIR MONITORING INSTRUMENTS

Principle of Detection and Monitoring Need	Instrument	Features	Limitations
Infrared Radiation <i>Monitoring Need:</i> Toxic Gas/ Vapors	Infrared Analyzer	<ul style="list-style-type: none"> Overcomes the limits of most infrared (IR) analyzers by use of a variable filter, can be used to scan through a portion of the spectrum to measure concentration of several gases or can be set at a particular wavelength to measure a specific gas Detects both organic and inorganic gases Portable but not as lightweight (32 lbs) as the PIDs or FIDs 	<ul style="list-style-type: none"> Less portable than other methods of gas/vapor detection Requires skilled technicians to operate and analyze results when positive identification is needed Interference by water vapor and carbon dioxide Most require AC power source Positive identification requires comparison of spectrum from strip chart recorder with published adsorption spectrum, infrared spectrum not available for all compounds Intrinsic safety is unit dependent, see manufacturer's literature
Chemical Reaction Producing a Color Change <i>Monitoring Need:</i> Toxic Gas/ Vapors	Indicator Tubes	<ul style="list-style-type: none"> Quantitative accuracies are variable Simple to use, and relatively inexpensive Real time/semi-real time results 	<ul style="list-style-type: none"> Low accuracy Subject to leakage during pumping Requires previous knowledge of gases/vapors in order to select the appropriate detector tube Some chemicals interfere with color reaction to read false positive Temperature and humidity may affect readings
Electrochemical Cell <i>Monitoring Need:</i> Toxic Gas/ Vapors Specific Atmospheres	Toxic Atmosphere Monitor	<ul style="list-style-type: none"> Ease of operation Small, compact, lightweight Audible alarm upon exceeding pre-set action level or Threshold Limit Value (TLV) Certain units have digital readout Generally compound-specific Certain units interface with data logger 	<ul style="list-style-type: none"> Cross sensitivity Slow response/recovery after exposure to high contamination levels Limited number of chemicals detected
Metal-Oxide Semiconductor <i>Monitoring Need:</i> Toxic Gas/ Vapors	Toxic Atmosphere Monitor	<ul style="list-style-type: none"> Ease of operation Small, compact, lightweight Audible alarm upon exceeding present action level or TLV Certain units have digital readout Certain units interface with data logger Nonspecific gas and vapor detection for some organics and inorganics 	<ul style="list-style-type: none"> Cross sensitivity Slow response/recovery after exposure to high contamination levels

TABLE 1 (CONT'D)
SUMMARY OF DIRECT-READING AIR MONITORING INSTRUMENTS

Principle of Detection and Monitoring Need	Instrument	Features	Limitations
Scintillation Detector <i>Monitoring Need: Radiation</i>	Radiation Meters	<ul style="list-style-type: none"> ◆ Measures radiation in R/hr or fractions thereof (gamma) (battery operated) ◆ Probe provides remote sensing capabilities ◆ Accuracy and sensitivity varies considerably with manufacturer and type of meter ◆ A variety of meters are available. Some measure total ionizing radiation; others are specific for gamma, alpha, or a combination of two or more types 	<ul style="list-style-type: none"> ◆ Some meters do not determine type of radiation <p>NOTE: Initial entry surveys should focus on the presence of gamma radiation. If alpha or beta are suspected, consult your health physicist.</p>
Gold Film Sensor <i>Monitoring Need: Mercury Vapor</i>	Mercury Vapor Analyzer	<ul style="list-style-type: none"> ◆ Compound specific; has survey and sample modes ◆ 0.001 mg/m³ detection limit ◆ Provides sensor saturation readout; saturated sensor cleaning capabilities ◆ Can be used with dosimeters for on-site dosimetry ◆ Microprocessor serves reading; automatically re-zeros ◆ Certain units have data logging capabilities ◆ 5-hour battery life 	<ul style="list-style-type: none"> ◆ Requires yearly <u>factory</u> recalibration ◆ Short battery life ◆ Requires AC power for Heat Cleaning Cycle

Sources: Mathamel, 1981; Spittler, 1980; McEnery, 1982; National Mine Service Company, 1980; Gas-Tech, 1980; Enmet Corporation, 1979; Foxboro Analytical, 1982; HNU Systems, 1982, 1991; Photovac International, Inc., 1989; Jerome, 1990; MIE, 1990.

TABLE 2
COMMON AIR SAMPLING METHODS AND MEDIA USED BY EPA/ERT¹

CONTAMINANT	AIR SAMPLING METHODS	FLOW RATE	COLLECTION MEDIA	SAMPLE DURATION (HOURS)
Hydrocarbons. BP 36-126 Deg C Aromatic Halogenated	NIOSH 1500 NIOSH 1501 NIOSH 1003	1 L/m 1 L/m 1 L/m	Charcoal	2-8
Inorganic Acids	NIOSH 7903	1 L/m	Silica Gel	2-8
Alcohols	NIOSH 1402	0.5 L/m	Charcoal	2-8
Acetic Acid	NIOSH 1603	1 L/m	Charcoal	2-8
Acetaldehyde	NIOSH 2538	1 L/m	2-Hydroxymethyl (2-HMP) Pipendine on XAD-2 Resin	2-8
Aliphatic Amines	NIOSH 2010	1 L/m	Silica Gel	8
Aromatic Amines	NIOSH 2002	1 L/m	Silica Gel	8
Volatile Organic Compounds	EPA TO1 and TO2	20 cc/m	Tenax/Carbon Molecular Sieve (CMS)	1-2
Volatile Organic Compounds	EPA TO14	Grab 10-50 cc/m	Summa Canister Summa Canister with Critical Orifice	Grab, 4-12
Polynuclear Aromatic Hydrocarbons (PAH)	NIOSH 5515	2.5 L/m or 5 L/m	XAD-2 Resin Tube with 37 mm 2 um Teflon [®] Filter with Polytetrafluoroethylene (PTFE) O- Ring Support	2-8
PAH	NIOSH 5506	260 L/m	2" x 1" Polyurethane Foam (PUF) with 50 grams XAD Resin	8-12
Pesticide/PCBs	Lewis and McCleod, Modified EPA TO4	3.5 L/m	2" x 3" PUF with Glass Fiber Filter	2-8
Dioxin ²	EPA TO9	260 L/m	2" x 3" PUF and Glass Fiber Filter	72
Metals	NIOSH 7300	3 L/m	0.8 um Mixed Cellulose Ester Filter (MCEF)	2-8
Formaldehyde	NIOSH 3500	1 L/m	1 um PTFE Filter and 2 Impingers, Each with 20 ml of 1 percent Sodium Bisulfite Solution	2-8
Formaldehyde	NIOSH 2541	0.1 L/m	10 percent 2-HMP on XAD-2 Resin	4-8

¹ This table is to be considered a guideline only. NIOSH methods were developed for indoor industrial use. Most NIOSH methods cited here have modified flow rates for use in outdoor ambient conditions. Sample duration should reflect extent of work shift when used in personal monitoring. If area sampling is being conducted for site characterization, sample durations may need to be modified to achieve desired detection limits.

² For dioxin, method is for area sampling only.

Note: OSHA analytical methods should also be evaluated for appropriate, applicable use. Most are available on OSHA's Computerized Information System (OCIS).

Information Sources

Federal Regulations

The OSHA HAZWOPER regulations are codified at 29 CFR 1910.120 (54 FR 9294 and 55 FR 14072). Subpart Z, Toxic and Hazardous Substances, can be found at 29 CFR 1910.1000.

The EPA HAZWOPER regulations are codified at 40 CFR 311 (54 FR 26654).

Computer Software

Air Methods Database (EPA/Environmental Response Team, Edison, NJ).

Available on the Cleanup Information electronic bulletin board (CLU-IN), formerly OSWER BBS. For further information, call (301) 589-8366. Communications: No Parity, 8 Databits, 1 Stopbit, E Duplex.

EPA Health and Safety Planner: Software and User's Guide (EPA, OSWER Publication 9285.8-01, 1990).

Fact Sheets

Hazardous Waste Operations and Emergency Response: General Information and Comparison (EPA, OSWER Publication 9285.2-09FS, 1991).

Explains the scope and purpose of the HAZWOPER standards, and distinguishes the SARA Title I standards from regulations and consensus standards covering the same or similar subject matter.

Hazardous Waste Operations and Emergency Response: Uncontrolled Hazardous Waste Sites and RCRA Corrective Action (EPA, OSWER Publication 9285.2-08FS, 1991).

Explains the principle HAZWOPER requirements as they apply to employees engaged in hazardous waste operations and emergency response at uncontrolled hazardous waste sites, including employees who perform corrective actions at RCRA TSD facilities.

Hazardous Waste Operations and Emergency Response: RCRA TSD and Emergency Response Without Regard to Location (EPA, OSWER Publication 9285.2-07FS, 1991).

Describes the HAZWOPER planning, training, and medical surveillance requirements as they apply to emergency responders regardless of location, and employees who perform routine hazardous waste operations at RCRA TSD facilities.

Establishing Work Zones at Uncontrolled Hazardous Waste Sites (EPA, OSWER Publication 9285.2-06FS, 1991).

Defines the different work zones usually found at a hazardous waste site (i.e., Exclusion, Contamination Reduction, and Support) and provides information on selecting and maintaining work zones.

Hazardous Waste Operations and Emergency Response: Available Guidance (EPA, OSWER Publication 9285.2-10FS, 1993).

Provides a list and description of computer software, fact sheets, guidance documents, and ERT training programs that pertain to the worker protection standards.

General Health and Safety Guidance Documents

Standard Operating Safety Guides (EPA, OSWER Publication 9285.1-03, 1992).

Provide guidelines for use by any organization in developing specific operation safety procedures. These Guides should be adapted to address the safety criteria required for protection of response personnel from the hazards created by a specific operation or incident.

Standard Operating Procedures for Air Sampling and Monitoring at Emergency Responses (EPA, OSWER Publication 9285.2-03A, draft).

Describes the types and methods of air surveillance, procedures and equipment for air monitoring, and a method for analyzing organic solvents by gas chromatography.

Standard Operating Procedures for Site Safety Planning (EPA, OSWER Publication 9285.2-05, being updated).

Describes the general requirements for a site safety plan, discusses development and implementation of a site safety plan, and provides sample plans and a checklist.

Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities (NIOSH/OSHA/USCG/EPA, NIOSH Publication 85-115, GPO No. 017-033-00419-6, 1985).

Draft International Document on Guide to Portable Instruments for Assessing Airborne Pollutants Arising from Hazardous Wastes (U.S. National Working Group (NWG-4 OIML) Pilot Secretariat PS-17: "Measurement of Pollution." Reporting Secretariat RS-5: "Measurement of Hazardous Waste Pollution." ISBN: 0-936712-75-9).

Provides guidance for using portable instruments to assess airborne pollutants arising from hazardous waste.

Procedures for Conducting Air Pathway Analyses for Superfund Applications addresses a variety of issues relevant to the air impacts at Superfund sites in four volumes entitled:

Volume I: Application of Air Pathway Analyses for Superfund Applications (EPA, EPA-450/1-89-001, NTIS PB90 113374/AS, 1989).

Volume II: Estimation of Baseline Air Emissions at Superfund Sites (EPA, EPA-450/1-89-002, NTIS PB89 18053/AS, 1989).

Volume III: Estimation of Air Emissions from Clean-up Activities at Superfund Sites (EPA, EPA-450/1-89-003, NTIS PB89 180061/AS, 1989).

Volume IV: Procedures for Dispersion Modeling and Air Monitoring for Superfund Air Pathway Analysis (EPA, EPA-450/1-89-004, NTIS PB90 113382/AS, 1989).

Standard Air Sampling Method Documentation

OSHA Analytical Methods. The OSHA Technical Center maintains an updated data base of analytical testing methods. Printouts of analytical methods for individual chemicals are available by request. For more information about the data base, contact:

OSHA Technical Center
1781 South 300 West
Salt Lake City, UT 84115
(801) 487-0521

Occupational Exposure Sampling Strategy Manual (Leidel, N.A., K.A. Busch, and J.R. Lynch. U.S. Department of Health, Education, and Welfare, Publ.(NIOSH) pp. 77-173, 1979).

Manual of Analytical Methods (Volumes 1-3, 3rd Ed., with supplements) (NIOSH Publication 89-127, 1989).

Recommended Exposure Limit Documentation

1991-1992 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices (American Conference of Governmental Industrial Hygienists, 1991).

Guide to Occupational Exposure Values-1992 (American Conference of Governmental Industrial Hygienists, 1991).

NIOSH Pocket Guide to Chemical Hazards (NIOSH Publication 90-117, updated annually).

Contacts

The following contacts can provide additional information on air monitoring and air sampling at uncontrolled hazardous waste sites:

American Industrial Hygiene
Association (AIHA)
Washington, D.C.
2700 Prosperity Avenue
Suite 250
Fairfax, Virginia 22031
(703) 849-8888

U.S. EPA
Environmental Response Team
2890 Woodbridge Avenue,
Building 18 (MS-101)
Edison, NJ 08837-3679
(908) 321-6740
24-Hour Hotline: (908) 321-6660

OSHA
U.S. Department of Labor
200 Constitution Avenue, NW
Room N-3647
Washington DC 20210
(202) 219-8036
OSHA Notification Service
(Complaint Hotline) for Emergency
Situations: 1-800-321-6742

EPA REGIONAL OFFICES

EPA Region 1
Emergency Planning and Response Branch
60 Westview Street
Lexington, MA 02173
(617) 860-4367

EPA Region 2
Response and Prevention Branch
2890 Woodbridge Avenue, Raritan Depot
Building 209
Edison, NJ 08837
(908) 321-6656

EPA Region 3
Superfund Removal Branch
841 Chestnut Street, 9th Floor
Philadelphia, PA 19107
(215) 597-0992

EPA Region 4
Emergency Response and Removal Branch
345 Courtland Street, NE
1st Floor
Atlanta, GA 30365
(404) 347-3931

EPA Region 5
Emergency and Enforcement Response Branch
77 West Jackson Boulevard
Chicago, IL 60604
(312) 353-9295

EPA Region 6
Emergency Response Branch
1145 Ross Avenue, 9th Floor
Dallas, TX 75202-2733
(214) 655-2270

EPA Region 7
Emergency Planning and Response Branch
25 Funston Road, 2nd Floor
Kansas City, KS 66115
(913) 551-5037

EPA Region 8
Emergency Response Branch
999 18th Street, Suite 500
Denver, CO 80202-2405
(303) 924-7129

EPA Region 9
Field Operations Branch
75 Hawthorne Street
San Francisco, CA 94105
(415) 744-2353

EPA Region 10
Superfund Branch
1200 6th Avenue, 11th Floor
Seattle, WA 98101
(206) 553-1677

OSHA REGIONAL OFFICES

Region 1 (CT, MA, ME, NH, RI, VT)
133 Portland Street, 1st Floor
Boston, MA 12114
(617) 565-7164

Region 2 (NJ, NY, PR, VI)
201 Varick Street, Room 670
New York, NY 10014
(212) 337-2378

Region 3 (DC, DE, MD, PA, VA, WV)
Gateway Building, Suite 2100
3535 Market Street
Philadelphia, PA 19104
(215) 596-1201

Region 4 (AL, FL, GA, KY, MS, NC, SC, TN)
1375 Peachtree Street, N.E.
Suite 587
Atlanta, GA 30367
(404) 347-3573

Region 5 (IL, IN, MI, MN, OH, WI)
230 South Dearborn Street, Room 3244
Chicago, IL 60604
(312) 353-2220

Region 6 (AR, LA, NM, OK, TX)
525 Griffin Street, Room 602
Dallas, TX 75202
(214) 767-4731

Region 7 (IA, KS, MO, NE)
911 Walnut Street, Room 406
Kansas City, MO 64106
(816) 426-5861

Region 8 (CO, MT, ND, SD, UT, WY)
Federal Building, Room 1576
1961 Stout Street
Denver, CO 80294
(303) 844-3061

Region 9 (American Samoa, AZ, CA, Guam,
HI, NV, Trust Territories of the Pacific)
71 Stevenson Street, Room 415
San Francisco, CA 94105
(415) 744-6670

Region 10 (AK, ID, OR, WA)
1111 Third Avenue, Suite 715
Seattle, WA 98101-3212
(206) 553-5930



United States
Environmental Protection
Agency
Washington, DC 20460

Official Business
Penalty for Private Use
\$300